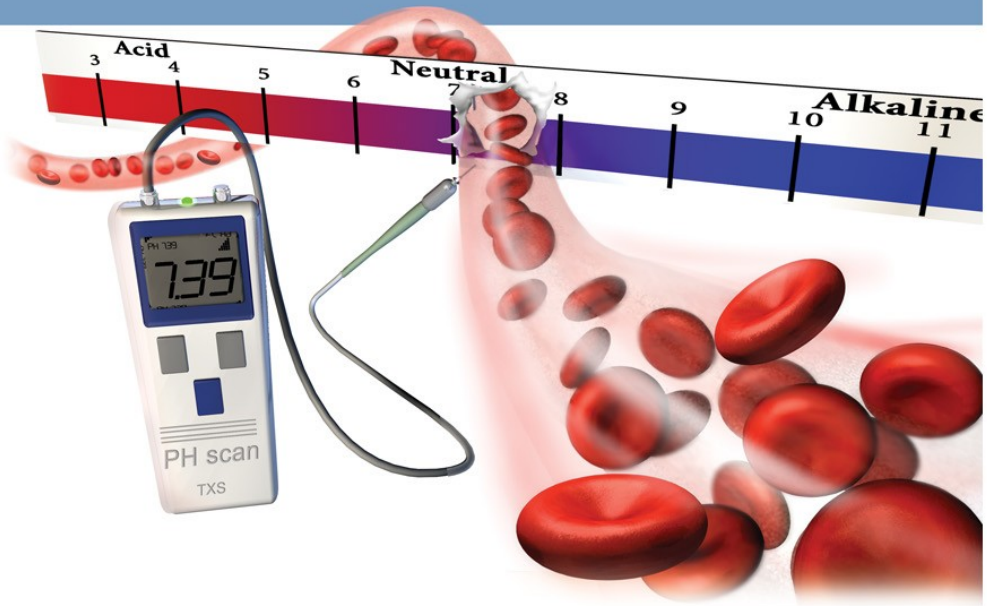
Chapter 15: Applications of Aqueous Equilibria - Titrations

GENERAL CHEMISTRY: ATOMS FIRST



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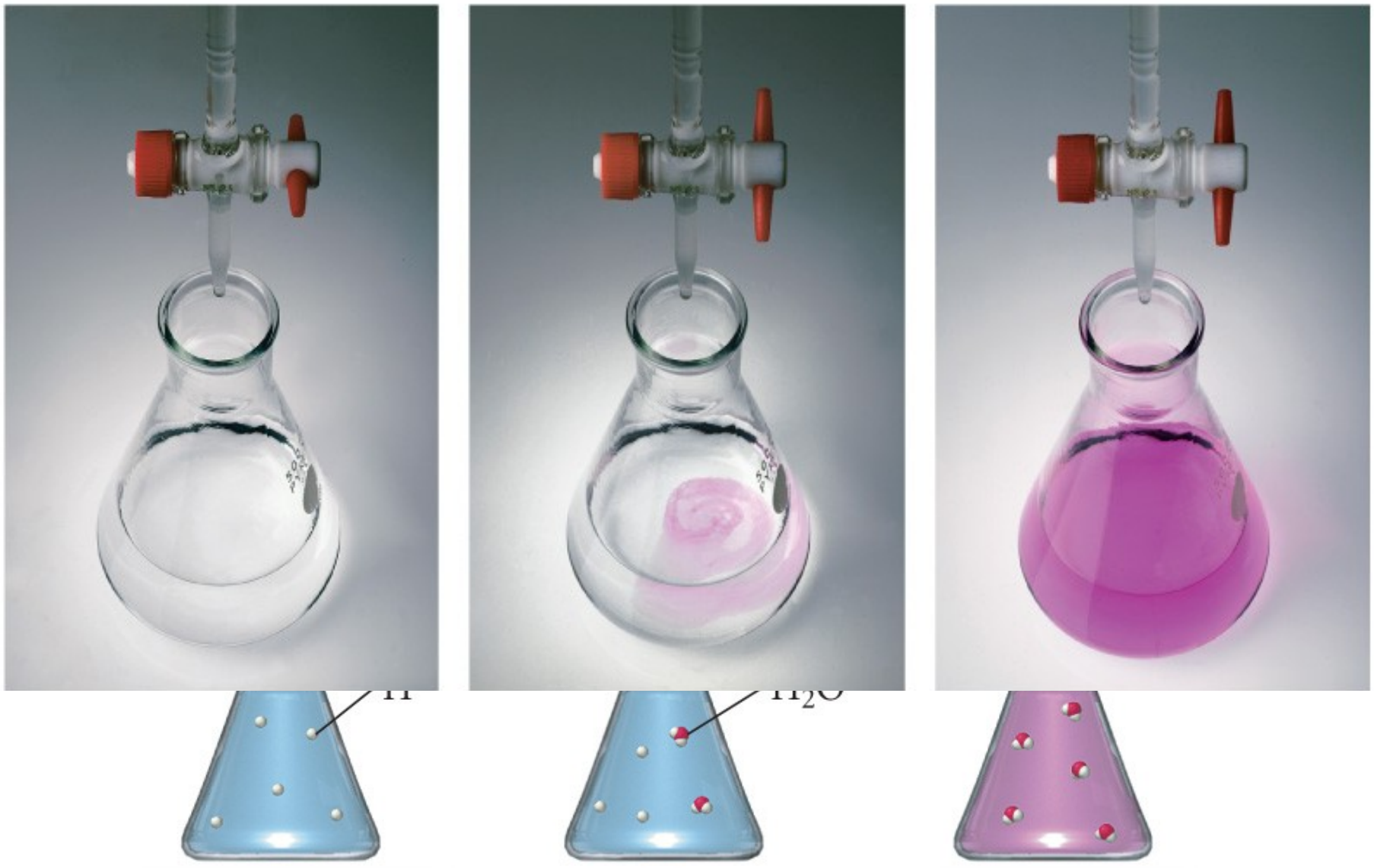
Titration

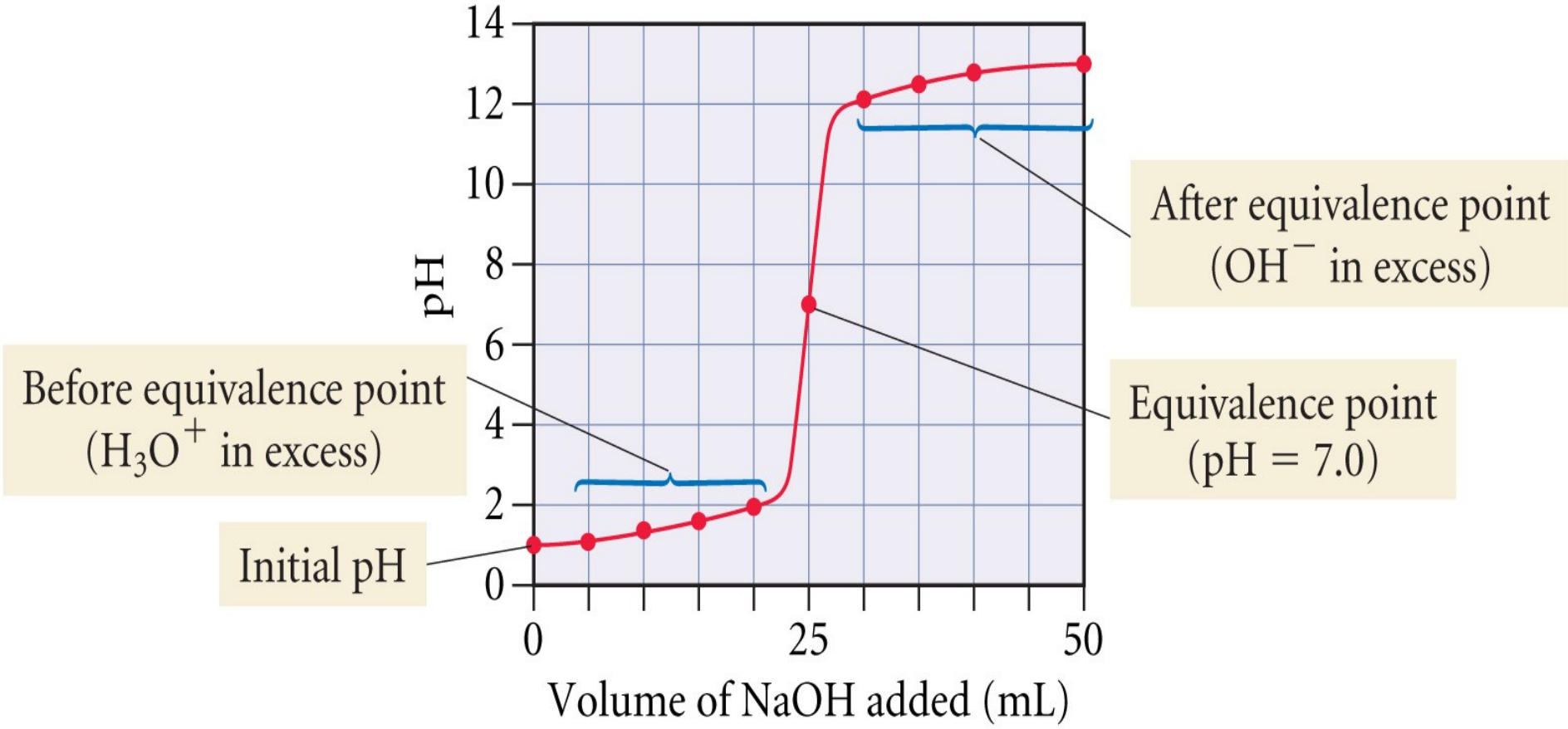
- in an acid-base titration, a solution of known concentration (**titrant**) is slowly added from a **burette** to a solution of unknown concentration in a flask until the reaction is complete
  - ✓ when the reaction is complete we have reached the **endpoint** of the titration
- an **indicator** may be added to determine the endpoint
  - ✓ an indicator is a chemical that changes color when the pH changes
- when the moles of H_3O^+ = moles of OH^-, the titration has reached its **equivalence point**


Beginning of titration
Equivalence point

The Titration Curve

- is a plot of pH vs. amount of added titrant
- the inflection point of the curve is the equivalence point of the titration
- prior to the equivalence point, the unknown solution in the flask is in excess, so the pH is closest to its pH
- the pH of the equivalence point depends on the pH of the salt solution
  - ✓ equivalence point of neutral salt, pH = 7
  - ✓ equivalence point of acidic salt, pH < 7
  - ✓ equivalence point of basic salt, pH > 7
- beyond the equivalence point, the known solution in the flask (from the burette) is in excess, so the pH approaches its pH

Titration Curve:
Known Strong Base Added to a Strong Acid



Strong Acid/Strong Base

Titration of 25 mL of 0.100 M HCl with 0.100 M NaOH

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(aq)}$$

- initial pH = -log(0.100) = 1.00
- initial moles HCl = (0.0250 L)(0.100 mol/L) = 2.50 x 10^{-3} mol HCl
- now add 5.0 mL (0.0050L) NaOH

$$0.0050\,\text{L NaOH} \times \frac{0.100\,\text{mol NaOH}}{1\,\text{L}}$$

$$= 5.0 \times 10^{-4}\,\text{mol NaOH}$$

$$5.0 \times 10^{-4}\,\text{mol NaOH} \times \frac{1\,\text{mol HCl}}{1\,\text{mol NaOH}}$$

$$= 5.0 \times 10^{-4}\,\text{mol HCl used}$$

Titration of 25 mL of 0.100 M HCl with 0.100 M NaOH

2.50×10^{-3} initial mol HCl $-$ 5.0×10^{-4} mol HCl used

$=2.00\times10^{-3}$ mol HCl excess

$$\frac{2.00\times10^{-3}\ \text{mol HCl excess}}{0.0250\ \text{L HCl} + 0.0050\ \text{L NaOH}}$$

$=0.0667$ M HCl $=[H_3O^+]$

$pH=-\log[H_3O^+]$ $pH=-\log(0.0667)=1.18$

Titration of 25 mL of 0.100 M HCl with 0.100 M NaOH

- when 25 mL NaOH added you reach the equivalence point
- no HCl and no NaOH present in flask, pH = 7.00
- after 30 mL (0.0300L) NaOH added, after the equivalence point:

$$0.0300\,\text{L NaOH} \times \frac{0.100\,\text{mol NaOH}}{1\,\text{L}}$$

$$= 3.00 \times 10^{-3}\,\text{mol NaOH}$$

$3.00 \times 10^{-3}\,\text{mol NaOH} - 2.50 \times 10^{-3}\,\text{mol NaOH}$

(amount of NaOH used to reach equivalence pt)

$= 5.0 \times 10^{-4}\,\text{mol NaOH}$ in excess

$$\frac{5.0 \times 10^{-4}\,\text{mol NaOH in excess}}{0.0250\,\text{L HCl} + 0.0300\,\text{L NaOH}}$$

$$= 0.00909\,\text{M NaOH} = [\text{OH}^-]$$

Titration of 25 mL of 0.100 M HCl with 0.100 M NaOH

$[OH^-] = 9.09 \times 10^{-3}$

$[H_3O^+][OH^-] = K_w$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{9.09 \times 10^{-3}} = 1.10 \times 10^{-12}$$

$pH = -\log[H_3O^+]$

$pH = -\log(1.10 \times 10^{-9}) = 11.96$

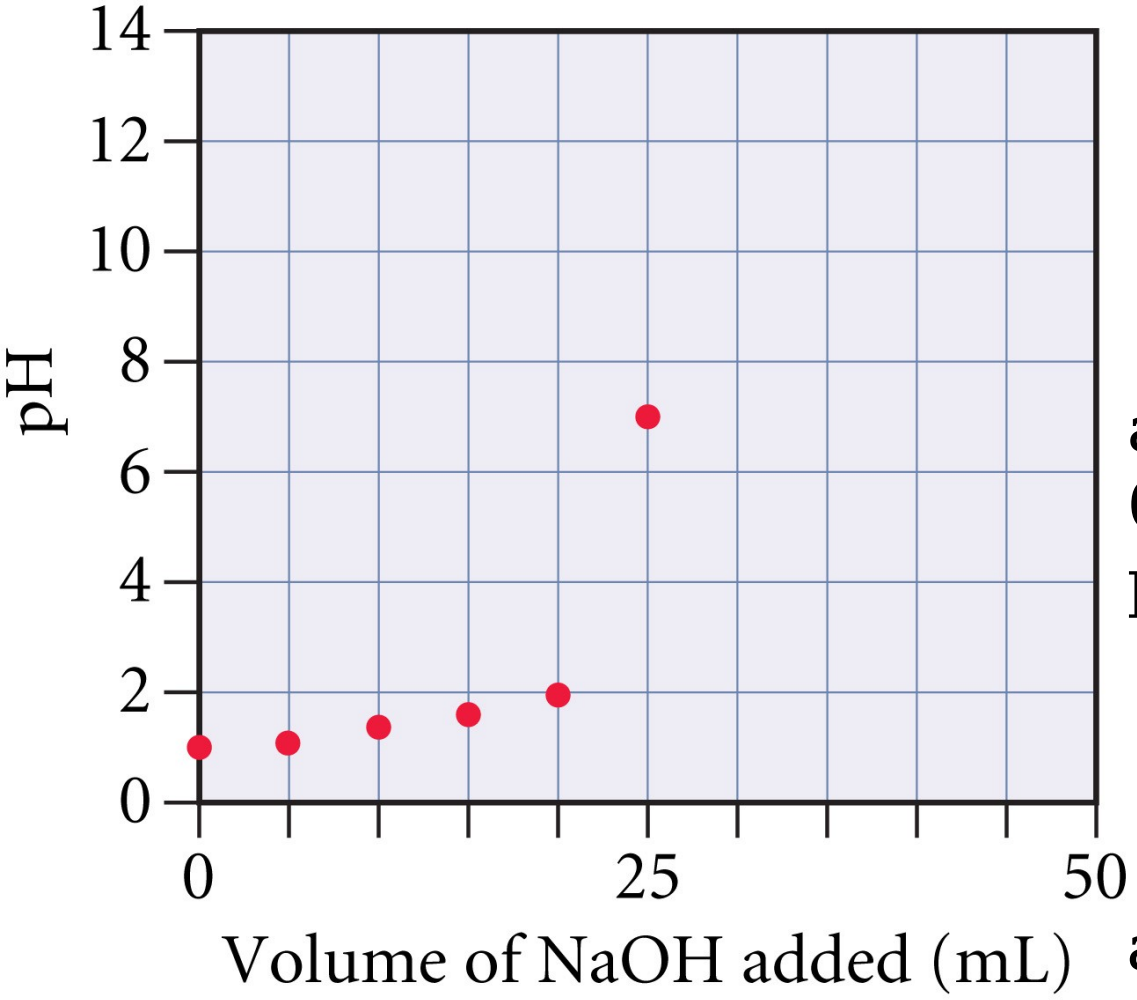
$pOH = -\log[OH^-]$

$pH = 14.00 - pOH$

$pOH = -\log(9.09 \times 10^{-3}) = 2.04$

$pH = 14.00 - 2.04 = 11.96$

Adding NaOH to HCl



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added 0.00 mL NaOH

0.00250 mol HCl

pH = 1.08

added 35.00 mL NaOH

pH = 11.96

0.00150 mol HCl

added 40.0 mL NaOH

0.00150 mol NaOH

pH = 12.36

added 25.0 mL NaOH

equivalence point

pH = 7.00

Titration of 25 mL of 0.100 M HCl with 0.100 M NaOH

- $HCHO_{2(aq)} + NaOH_{(aq)} \rightarrow NaCHO_{2\ (aq)} + H_2O_{(l)}$
- after equivalence point

$$\frac{\text{mol NaOH} - \text{excess}}{\text{L HCl} + \text{L NaOH}} = \text{M NaOH} = [OH^-]$$

$$\frac{5.0\times10^{-4}\ \text{mol NaOH}}{0.0250\ \text{L HCl} + 0.0300\ \text{L NaOH}} = 0.0091\ \text{M NaOH} = [OH^-]$$

$$[H_3O^+][OH^-] = K_w$$

$$[H_3O^+] = \frac{K_w}{[OH^-]}$$

$$= \frac{1\times10^{-14}}{9.1\times10^{-3}} = 1.10\times10^{-12}$$

$$pH = -\log[H_3O^+]$$

$$pH = -\log(1.10\times10^{-12}) = 11.96$$

Titrating Weak Acid with a Strong Base

- the initial pH is that of the weak acid solution
  - ✓calculate like a weak acid equilibrium problem
    - ➢e.g., 15.5 and 15.6
- before the equivalence point, the solution becomes a buffer
  - ✓calculate mol HA_{init} and mol A^-_{init} using reaction stoichiometry
  - ✓calculate pH with Henderson-Hasselbalch using mol HA_{init} and mol A^-_{init}
- half-neutralization pH = pK_a

Titrating Weak Acid with a Strong Base

- at the equivalence point, the mole HA = mol Base, so the resulting solution has only the conjugate base anion in it before equilibrium is established
  - ✓mol A^- = original mole HA
    - ➢calculate the volume of added base like Ex 4.8
  - ✓$[A^-]_{init}$ = mol A^-/total liters
  - ✓calculate like a weak base equilibrium problem
    - ➢e.g., 15.14
- beyond equivalence point, the OH is in excess
  - ✓$[OH^-]$ = mol MOH xs/total liters
  - ✓$[H_3O^+][OH^-]=1 \times 10^{-14}$

Titration of a weak acid, 25 mL of 0.100 M $HCHO_2$,with a strong base, 0.100 M NaOH

$$HCHO_{2(aq)} + NaOH_{(aq)} \rightarrow NaCHO_{2(aq)} + H_2O_{(l)}$$

$$K_a = 1.8 \times 10^{-4} = \frac{[CHO_2^-]\,[H_3O^+]}{[HCHO2]}$$

Titration of a weak acid, 25 mL of 0.100 M $HCHO_2$, with a strong base, 0.100 M NaOH

$$HCHO_{2(aq)} + H_2O_{(l)} \rightarrow CHO_2^-{}_{(aq)} + H_3O^+{}_{(aq)}$$

	$[HCHO_2]$	$[CHO_2^-]$	$[H_3O^+]$
initial	0.100	0.000	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	$0.100 - x$	x	x

$$K_a = 1.8 \times 10^{-4}$$

$$K_a = \frac{[CHO_2^-][H_3O^+]}{[HCHO_2]}$$

$$1.8\times10^{-4} = \frac{(x)(x)}{(0.100 - x)} = \frac{x^2}{0.100}$$

$$x = [H_3O^+] = 4.24\times10^{-3}\ M$$

$$\frac{4.2\times10^{-3}}{0.100}\times100\% = 4.2\% < 5\%$$

$$pH = -\log[H_3O^+]$$

$$= -\log(4.24\times10^{-3}) = 2.37$$

Titration of a weak acid, 25 mL of 0.100 M $HCHO_2$, with a strong base, 0.100 M NaOH

$$HCHO_{2(aq)} + NaOH_{(aq)} \rightarrow NaCHO_{2\ (aq)} + H_2O_{(l)}$$

- initial mol of $HCHO_2$ = 0.0250 L x 0.100 mol/L = 2.50×10^{-3}

add 5.0 mL NaOH

$$0.0050\ \text{L NaOH} \times \frac{0.100\ \text{mol NaOH}}{1\ \text{L}} = 5.0 \times 10^{-4}\ \text{mol NaOH}$$

	HA	A^-	OH^-
mols start	2.50E-3	0	0
mols added	-	-	5.0E-4
mols after	2.00E-3	5.0E-4	≈ 0

$$pH = pK_a + \log\left(\frac{\text{mol } CHO_2^-}{\text{mol } HCHO_2}\right)$$

given $K_a = 1.8 \times 10^{-4}$

$$pK_a = -\log K_a$$

$$= -\log\left(1.8 \times 10^{-4}\right) = 3.74$$

$$pH = 3.74 + \log\left(\frac{5.0 \times 10^{-4}}{2.00 \times 10^{-3}}\right)$$

$$pH = 3.14$$

Titration of a weak acid, 25 mL of 0.100 M $HCHO_2$, with a strong base, 0.100 M NaOH

- $HCHO_{2(aq)} + NaOH_{(aq)} \rightarrow NaCHO_{2\ (aq)} + H_2O_{(aq)}$
- initial mol of $HCHO_2$ = 0.0250 L x 0.100 mol/L = 2.50×10^{-3}
- at equivalence

$CHO_{2\ (aq)}^- + H_2O_{(l)} \Leftrightarrow HCHO_{2(aq)} + OH^-_{(aq)}$ added 25.0 mL NaOH

	HA	A^-	OH^-
mols Before	2.50E-3	0	0
mols added	-	-	2.50E-3
mols After	0	2.50E-3	≈ 0

$$0.0250\,\text{L NaOH} \times \frac{0.100\,\text{mol NaOH}}{1\,\text{L}}$$

$$= 2.50 \times 10^{-3}\,\text{mol NaOH}$$

$$\frac{2.50 \times 10^{-3}\,\text{mol } CHO_2^-}{2.50 \times 10^{-2}\,\text{L } HCHO_2 + 2.50 \times 10^{-2}\,\text{L NaOH}}$$

$$= 5.00 \times 10^{-2}\,\text{M } CHO_2^-$$

Titration of a weak acid, 25 mL of 0.100 M $HCHO_2$,with a strong base, 0.100 M NaOH**

- $HCHO_{2(aq)} + NaOH_{(aq)} \rightarrow NaCHO_{2\ (aq)} + H_2O_{(aq)}$
- initial mol of $HCHO_2$ = 0.0250 L x 0.100 mol/L = 2.50×10^{-3}
- at equivalence

$CHO_{2\ (aq)}^- + H_2O_{(l)} \Leftrightarrow HCHO_{2(aq)} + OH^-_{(aq)}$

	$[HCHO_2]$	$[CHO_2^-]$	$[OH^-]$
initial	0	0.0500	≈ 0
change	$+x$	$-x$	$+x$
equilibrium	x	5.00E-2-x	x

$K_b = 5.6 \times 10^{-11}$

$$K_{b,CHO_2^-} = \frac{K_w}{K_a} = \frac{1\times10^{-14}}{1.8\times10^{-4}} = 5.6\times10^{-11}$$

$$K_b = \frac{[HCHO_2][OH^-]}{[CHO_2^-]}$$

$$5.6\times10^{-11} = \frac{(x)(x)}{(0.0500 - x)} = \frac{x^2}{0.0500}$$

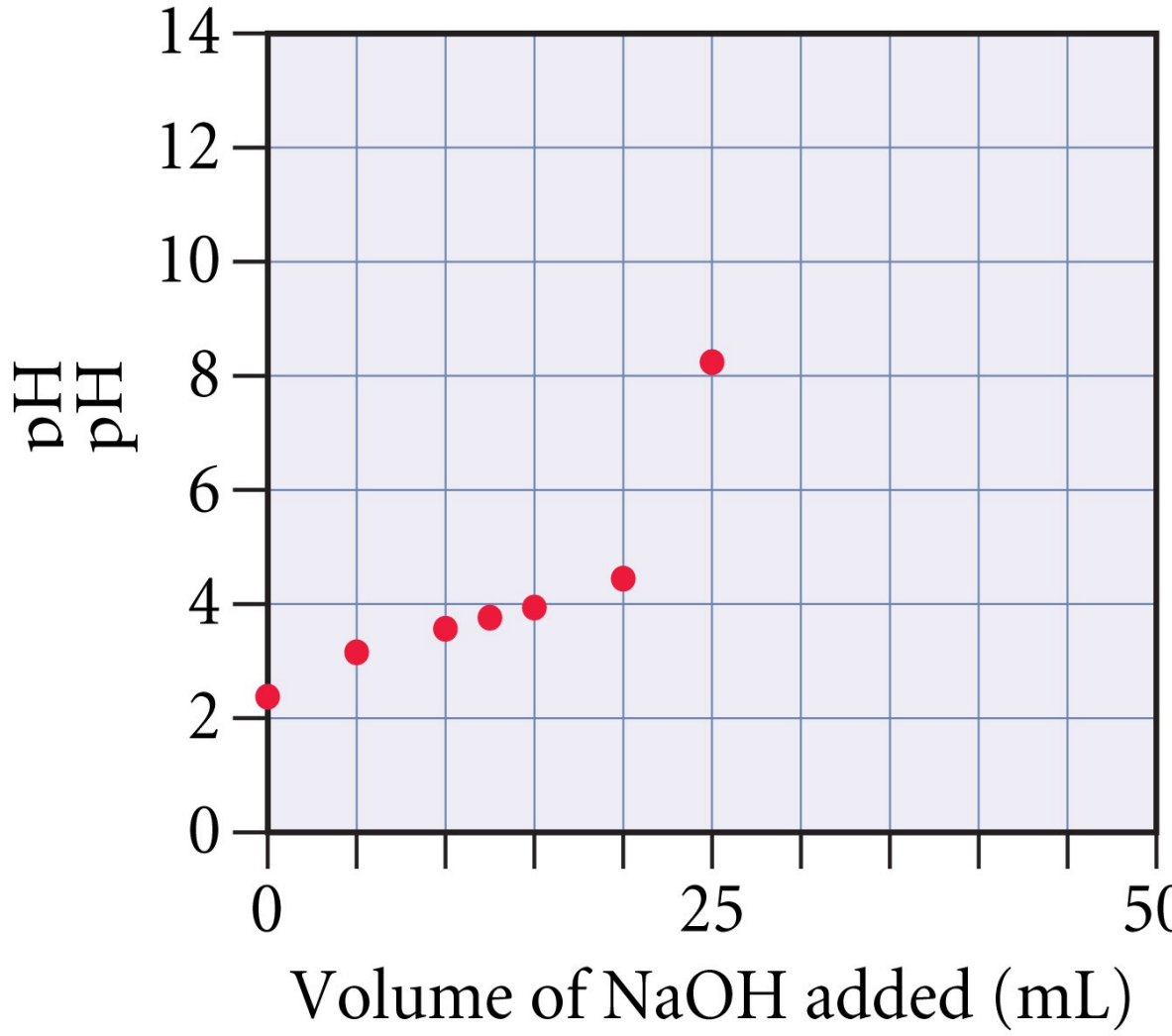
$$x = [OH^-] = 1.7\times10^{-6}\ M$$

$[OH^-] = 1.7 \times 10^{-6}$ M

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1\times10^{-14}}{1.7\times10^{-6}} = 5.9\times10^{-9}$$

$$pH = -\log[H_3O^+] = -\log(5.9\times10^{-9}) = 8.23$$

Adding NaOH to $HCHO_2$



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added 50.0 mL NaOH

0.00250 mol $HCHO_2$ xs

0.00250 mol CHO_2^-

$[CHO_2^-] = 0.0500\ M$

pH = 8.24

added 40.0 mL NaOH

0.00150 mol NaOH xs

pH = 12.36

alf-neutralization

added 25.0 mL NaOH

0.00250 mol NaOH xs

pH = 3.92

dded 20.0 mL NaOH

.00050 mol $HCHO_2$

pH = 4.34

A 40.0 mL sample of 0.100 M HNO_2 is titrated with 0.200 M KOH. Calculate the volume of KOH at the equivalence point

Write an equation for the reaction for B with HA.
Use Stoichiometry to determine the volume of added B

$$HNO_2 + KOH \rightarrow NO_2^- + H_2O$$

$$40.0\,mL \times \frac{0.001\,L}{1\,mL} = 0.0400\,L$$

$$0.0400\,L\,HNO_2 \times \frac{0.100\,mol\,HNO_2}{1\,L\,NO_2} \times \frac{1\,mol\,KOH}{1\,mol\,HNO_2} \times \frac{1\,L\,KOH}{0.200\,mol\,KOH}$$

$$= 0.0200\,L\,KOH$$

$$0.0200\,L \times \frac{1\,mL}{0.001\,L} = 20.0\,mL$$

A 40.0 mL sample of 0.100 M HNO_2 is titrated with 0.200 M KOH. Calculate the pH after adding 5.00 mL KOH

Write an equation for the reaction for B with HA.
Determine the moles of HA_{before} & moles of added B
Make a stoichiometry table and determine the moles of HA in excess and moles A^- made

$$HNO_2 + KOH \rightarrow NO_2^- + H_2O$$

$$40.0\,mL \times \frac{0.001\,L}{1\,mL} \times \frac{0.100\,mol\,HNO_2}{1\,L} = 0.00400\,mol\,HNO_2$$

$$5.00\,mL \times \frac{0.001\,L}{1\,mL} \times \frac{0.200\,mol\,KOH}{1\,L} = 0.00100\,mol\,KOH$$

	HNO_2	NO_2^-	OH^-
mols Before	0.00400	0	≈ 0
mols added	-	-	0.00100
	0.00300	0.00100	

A 40.0 mL sample of 0.100 M HNO_2 is titrated with 0.200 M KOH. Calculate the pH after adding 5.00 mL KOH.

Write an equation for the reaction of HA with H_2O
Determine K_a and pK_a for HA
Use the Henderson-Hasselbalch Equation to determine the pH

$$HNO_2 + H_2O \Leftrightarrow NO_2^- + H_3O^+$$

Table 15.5 $K_a = 4.6 \times 10^{-4}$

$$pK_a = -\log K_a = -\log\left(4.6\times10^{-4}\right) = 3.15$$

$$pH = pK_a + \log\left(\frac{NO_2^-}{HNO_2}\right)$$

$$pH = 3.15 + \log\left(\frac{0.00100}{0.00300}\right) = 2.67$$

	HNO_2	NO_2^-	OH^-
mols Before	0.00400	0	≈ 0
mols added	-	-	0.00100

A 40.0 mL sample of 0.100 M HNO_2 is titrated with 0.200 M KOH. Calculate the pH at the half-equivalence point

Write an equation for the reaction for B with HA.
Determine the moles of HA_{before} & moles of added B
Make a stoichiometry table and determine the moles of HA in excess and moles A^- made

$$HNO_2 + KOH \rightarrow NO_2^- + H_2O$$

$$40.0\,mL \times \frac{0.001\,L}{1\,mL} \times \frac{0.100\,mol\,HNO_2}{1\,L} = 0.00400\,mol\,HNO_2$$

at half-equivalence, moles KOH = ½ mole HN

	HNO_2	NO_2^-	OH^-
mols Before	0.00400	0	≈ 0
mols added	-	0.00200	0.00200

A 40.0 mL sample of 0.100 M HNO_2 is titrated with 0.200 M KOH. Calculate the pH at the half-equivalence point.

Write an equation for the reaction of HA with H_2O
Determine K_a and pK_a for HA
Use the Henderson-Hasselbalch Equation to determine the pH

$$HNO_2 + H_2O \Leftrightarrow NO_2^- + H_3O^+$$

Table 15.5 $K_a = 4.6 \times 10^{-4}$

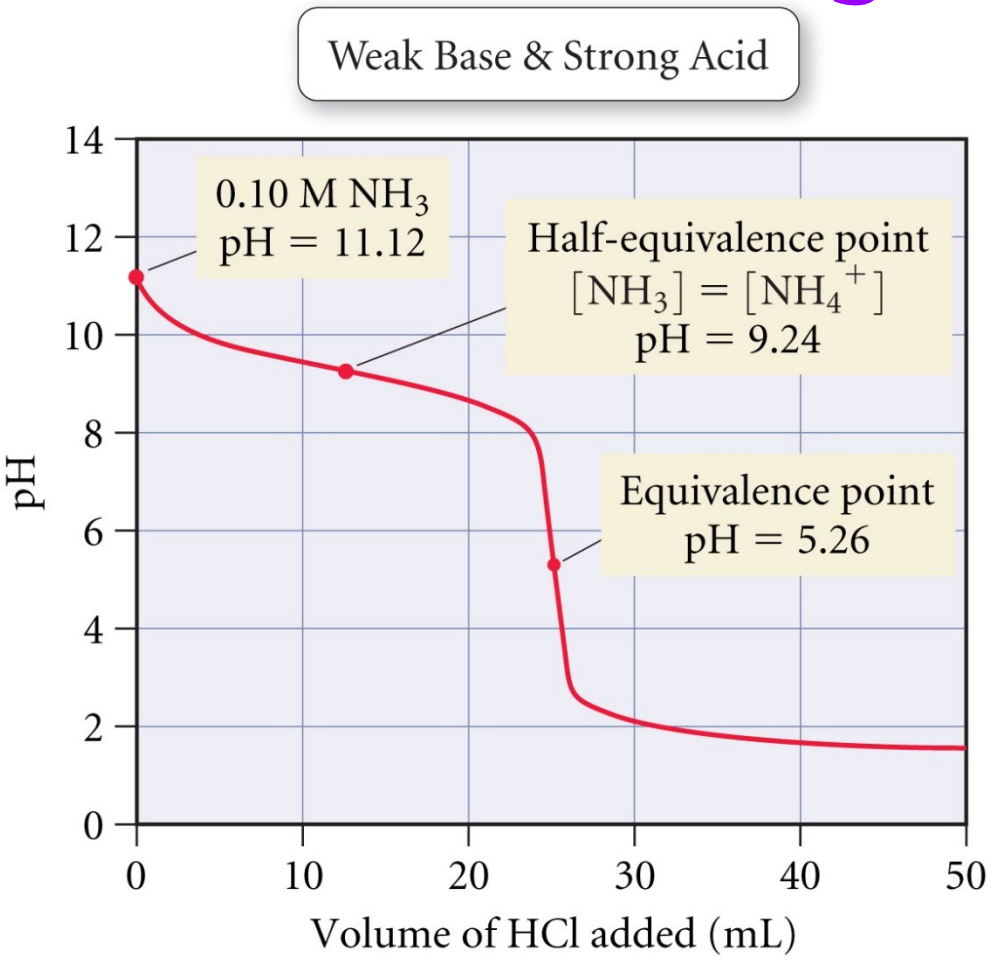
$$pK_a = -\log K_a = -\log\left(4.6\times10^{-4}\right) = 3.15$$

$$pH = pK_a + \log\left(\frac{NO_2^-}{HNO_2}\right)$$

$$pH = 3.15 + \log\left(\frac{0.00200}{0.00200}\right) = 3.15$$

	HNO_2	NO_2^-	OH^-
mols Before	0.00400	0	≈ 0
mols added	-	-	0.00200

Titration Curve of a Weak Base with a Strong Acid



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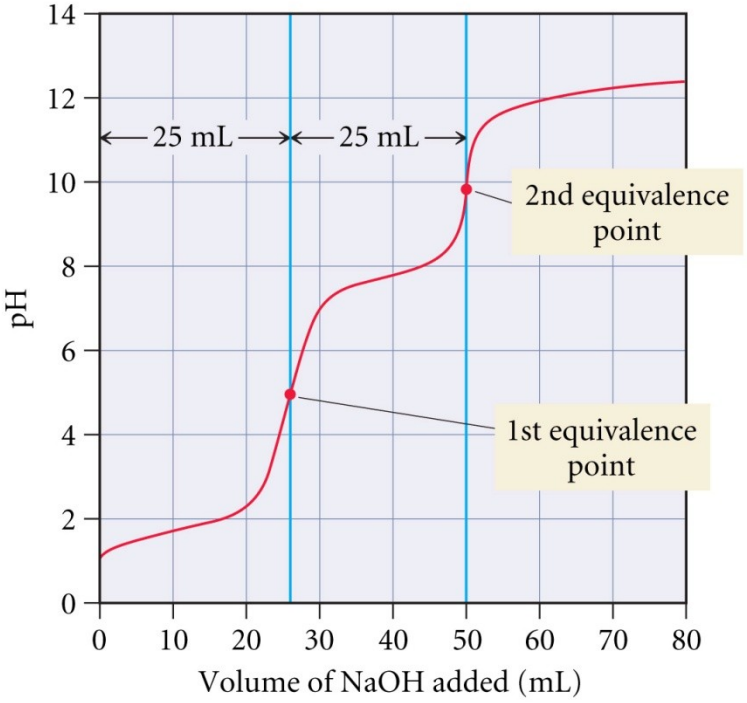
Titration of a Polyprotic Acid

- if $K_{a1} >> K_{a2}$, there will be two equivalence points in the titration
  - ✓the closer the K_a's are to each other, the less distinguishable the equivalence points are

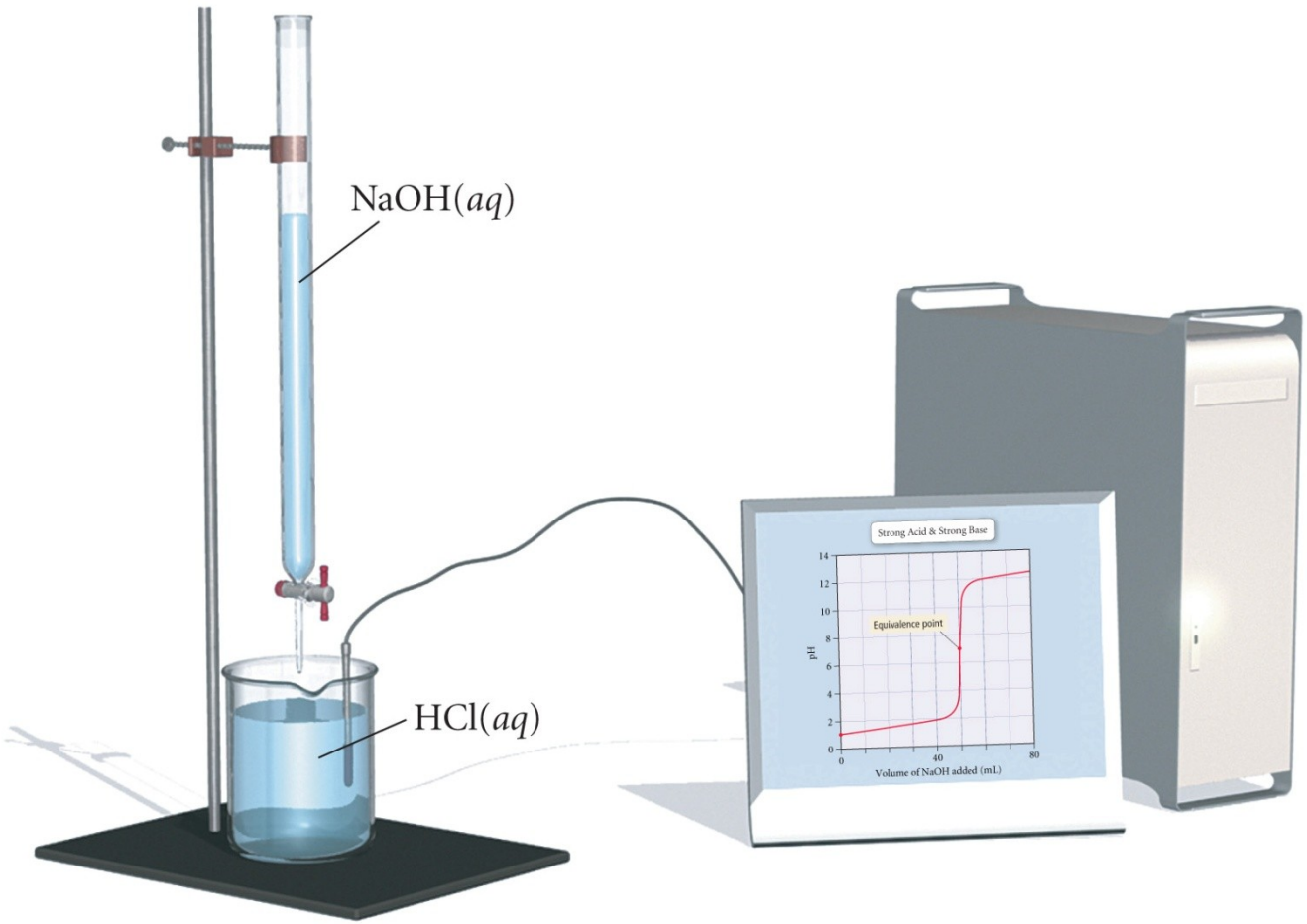


titration of 25.0 mL of 0.100 M H_2SO_3 with 0.100 M NaOH

Monitoring pH During a Titration

- the general method for monitoring the pH during the course of a titration is to measure the conductivity of the solution due to the $[H_3O^+]$
  - ✓ using a probe that specifically measures just H_3O^+
- the **endpoint** of the titration is reached at the equivalence point in the titration – at the inflection point of the titration curve
- if you just need to know the amount of titrant added to reach the endpoint, we often monitor the titration with an **indicator**

Monitoring pH During a Titration



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Monitoring a Titration with an Indicator

- for most titrations, the titration curve shows a very large change in pH for very small additions of base near the equivalence point
- an indicator can therefore be used to determine the endpoint of the titration if it changes color within the same range as the rapid change in pH
  - ✓ pK_a of H-Indicator ≈ pH at equivalence point

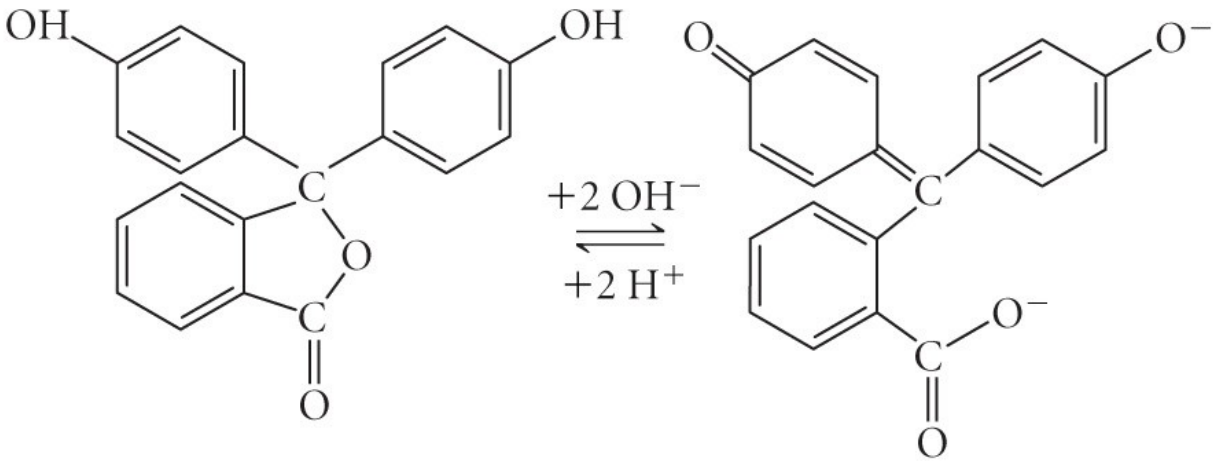
Indicators

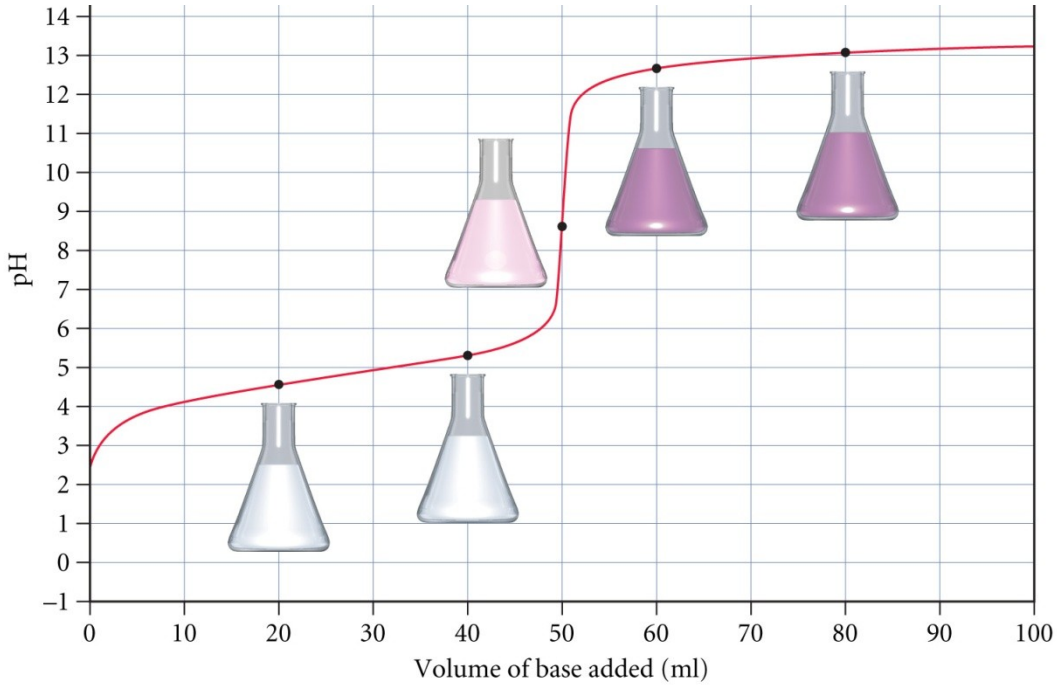
- many dyes change color depending on the pH of the solution
- these dyes are weak acids, establishing an equilibrium with the H_2O and H_3O^+ in the solution

$$H\text{-}Ind_{(aq)} + H_2O_{(l)} \Leftrightarrow Ind^-_{(aq)} + H_3O^+_{(aq)}$$

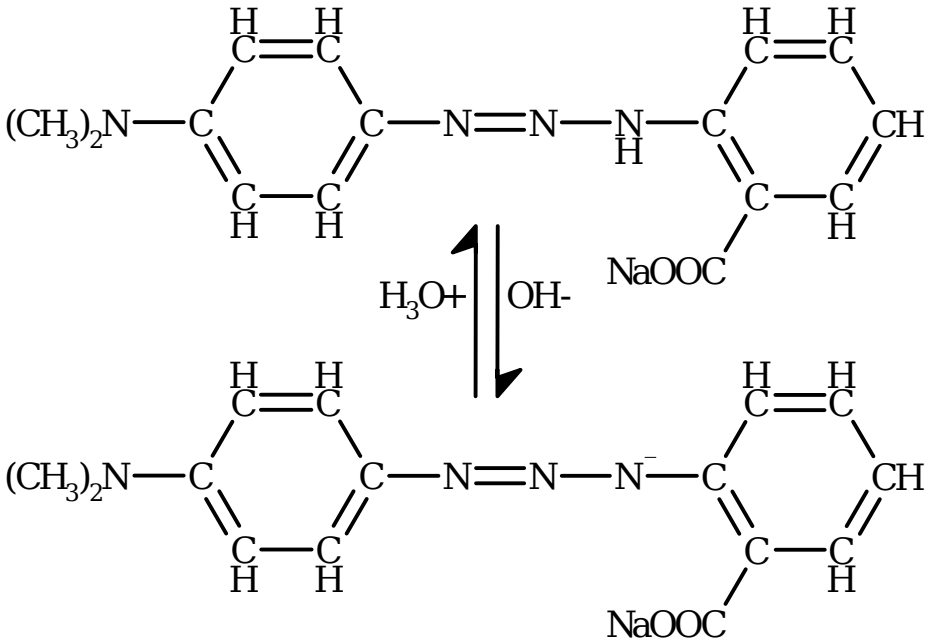
- the color of the solution depends on the relative concentrations of Ind^-:HInd
  - ✓ when Ind^-:H-Ind ≈ 1, the color will be mix of the colors of Ind^- and HInd
  - ✓ when Ind^-:H-Ind > 10, the color will be mix of the colors of Ind^-
  - ✓ when Ind^-:H-Ind < 0.1, the color will be mix of the colors of H-Ind

Phenolphthalein





Methyl Red



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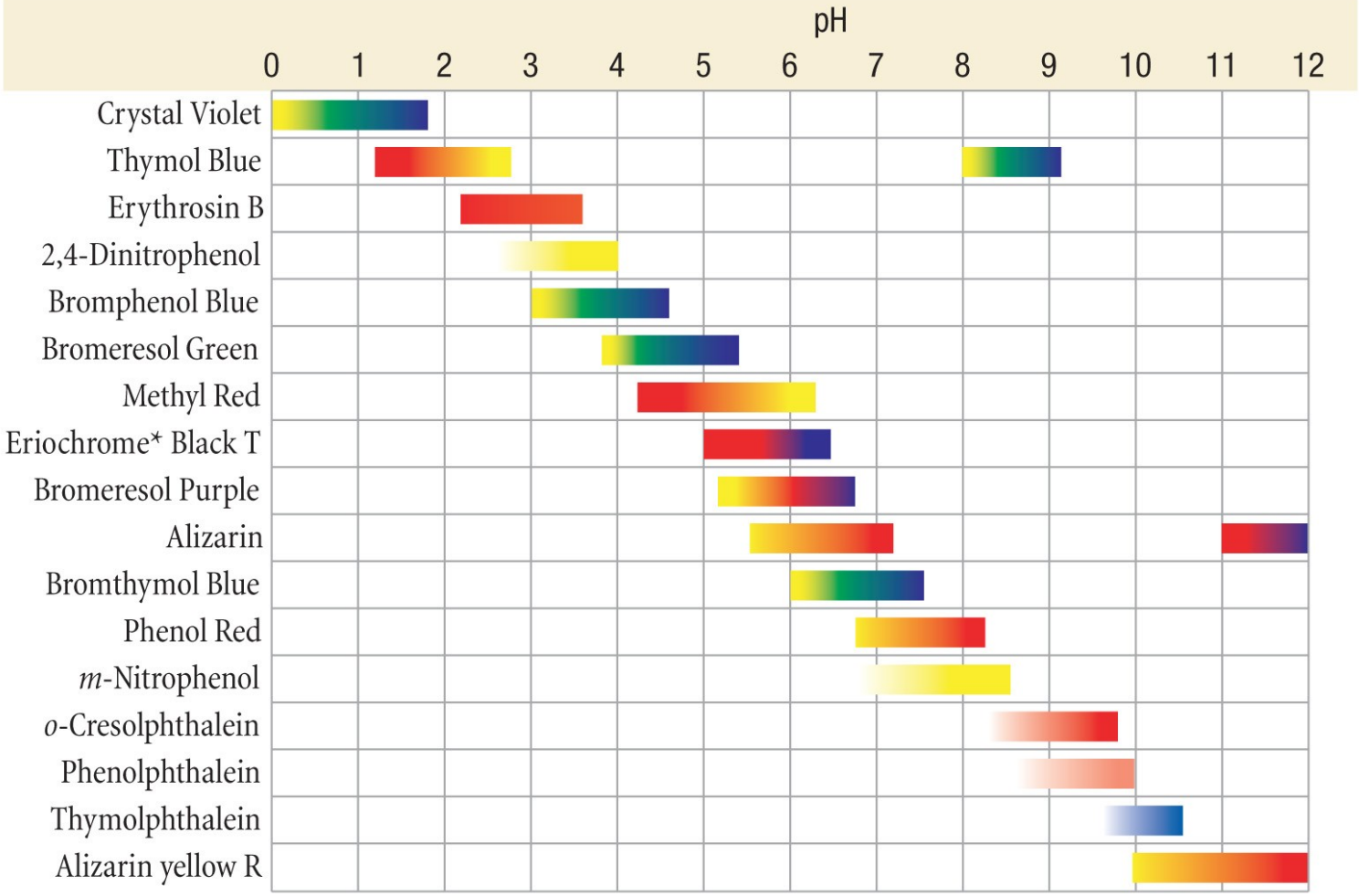
Acid-Base Indicators

TABLE 16.1 Ranges of Color Changes for Several Acid-Base Indicators



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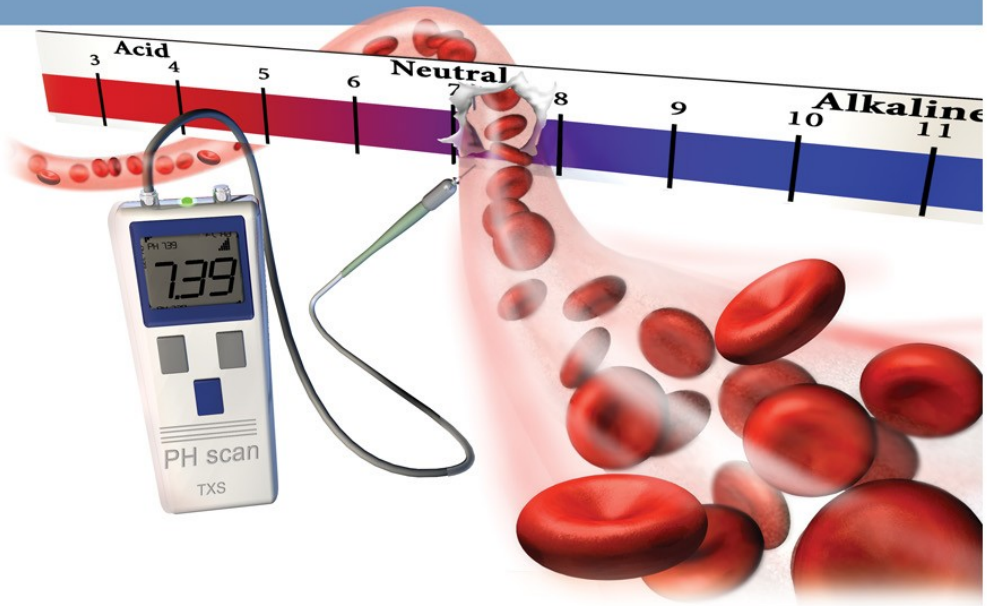
Chapter 15: Applications of Aqueous Equilibria-Buffers

GENERAL CHEMISTRY: ATOMS FIRST



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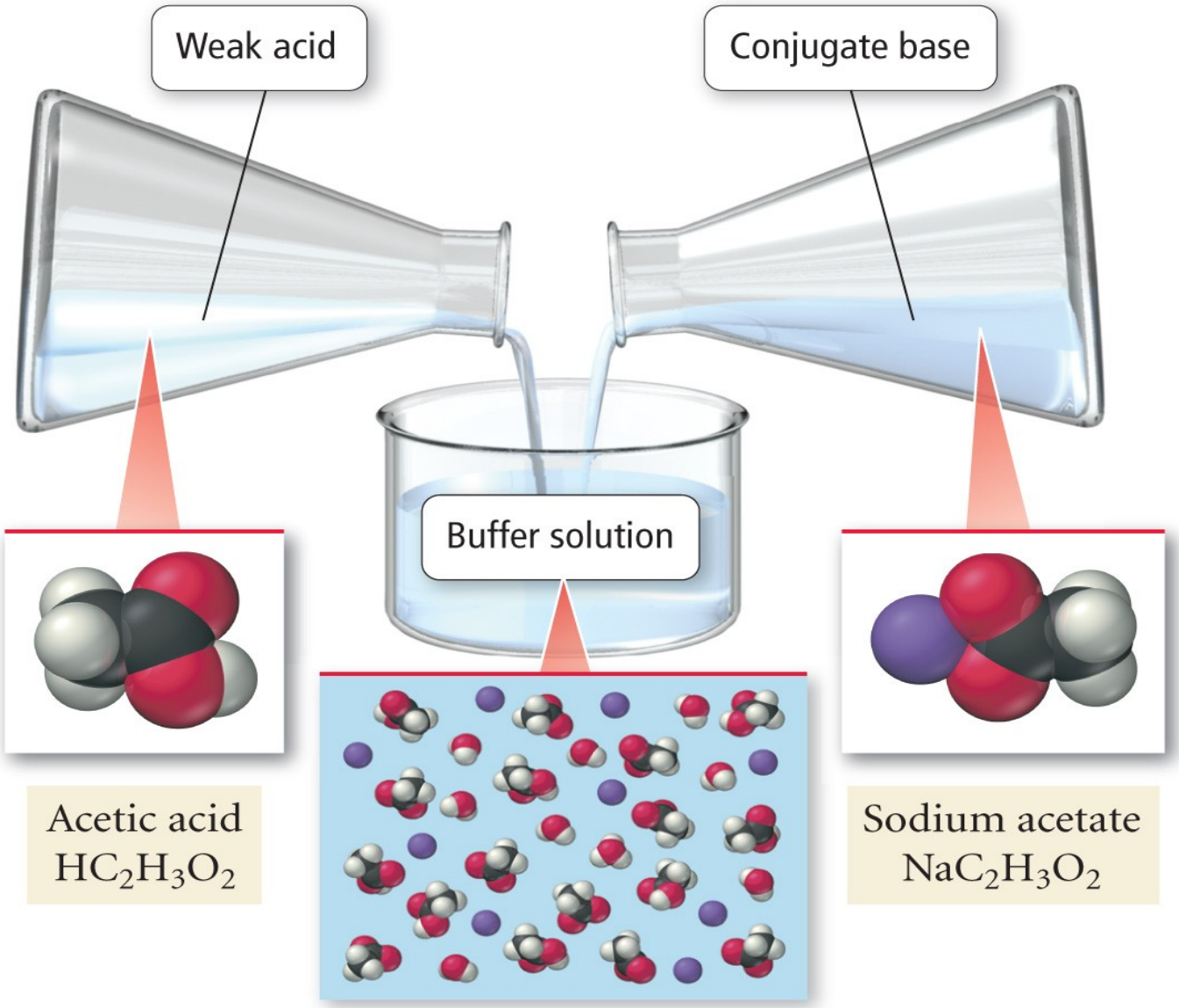
Buffers

- **buffers** are solutions that resist changes in pH when an acid or base is added
- they act by neutralizing the added acid or base
- there is a limit to their neutralizing ability, eventually the pH changes
- Solution made by mixing a weak acid with a soluble salt containing its conjugate base anion

Formation of an Acid Buffer

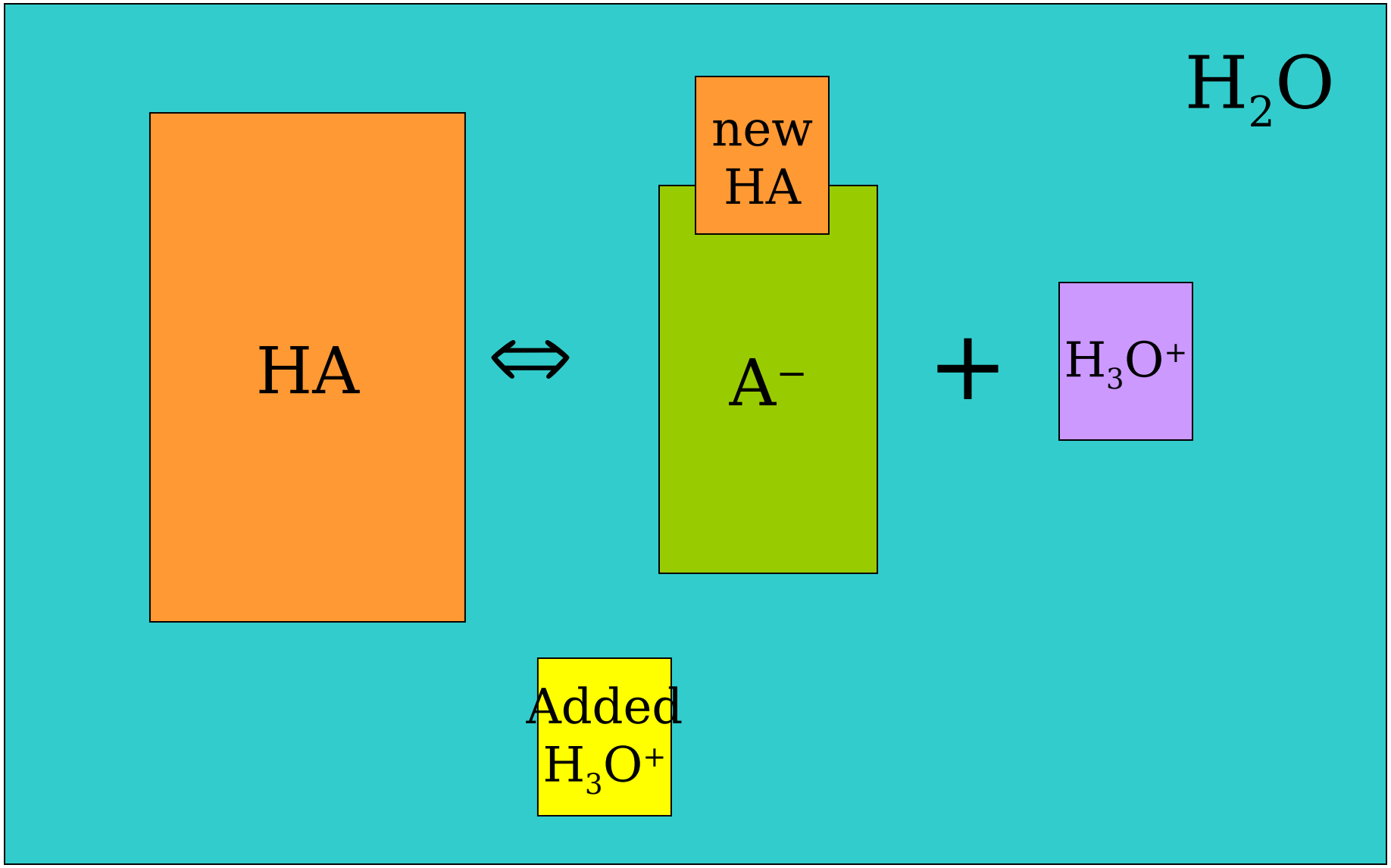


How Acid Buffers Work

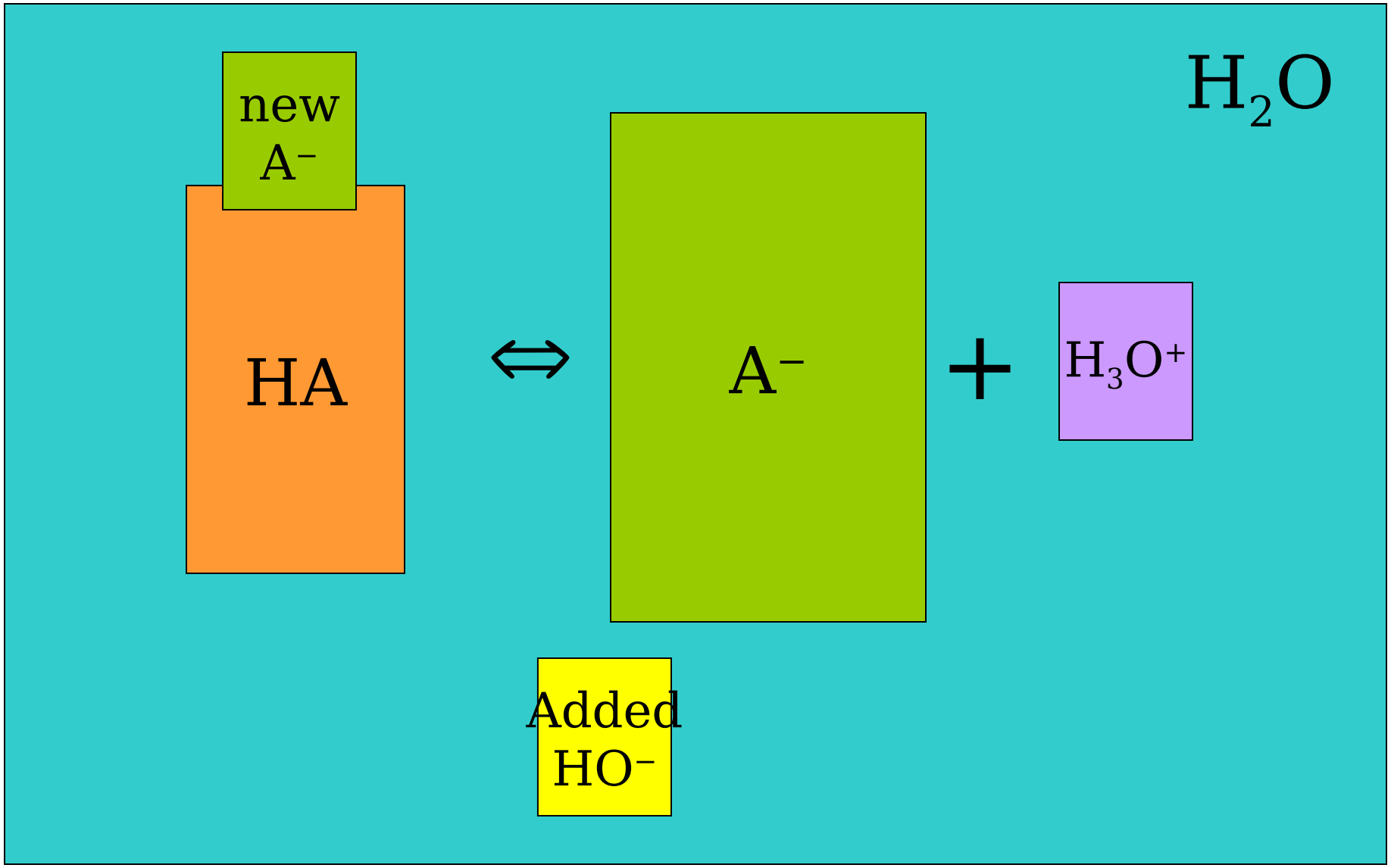
$$HA_{(aq)} + H_2O_{(l)} \Leftrightarrow A^-_{(aq)} + H_3O^+_{(aq)}$$

- buffers follow Le Châtelier's Principle
- buffers contain significant amount of weak acid, HA
  - ✓ The HA molecules react with added base to neutralize it
  - ✓ the H_3O^+ combines with OH^- to make H_2O
  - ✓ H_3O^+ is then replaced by the shifting equilibrium
- buffer solutions also contain significant amount of conjugate base anion, A^-
  - ✓ The A^- molecules react with added acid to make more HA and keep H_3O^+ constant

How Buffers Work



How Buffers Work



Common Ion Effect

$$HA_{(aq)} + H_2O_{(l)} \Leftrightarrow A^-_{(aq)} + H_3O^+_{(aq)}$$

Le Châtelier's Principle

- adding a salt, NaA, containing the acid anion, shifts the position of equilibrium to the left (A^- is the conjugate base of the acid)
- this lowers the H_3O^+ ion concentration and causes the pH to be higher

Common Ion Effect

pH = 2.9

0.100 M
$HC_2H_3O_2$

pH = 8.9

0.100 M
$NaC_2H_3O_2$

pH = 4.7

0.100 M $HC_2H_3O_2$
0.100 M $NaC_2H_3O_2$

What is the pH of a buffer that is 0.100 M $HC_2H_3O_2$ and 0.100 M $NaC_2H_3O_2$?

K_a for $HC_2H_3O_2 = 1.8 \times 10^{-5}$

Write the reaction for the acid with water
Construct an ICE table for the reaction
Enter the initial concentrations – assuming the $[H_3O^+]$ from water is ≈ 0

$$H_2O + HC_2H_3O_2 \Leftrightarrow C_2H_3O_2^- + H_3O^+$$

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.100	0.100	≈ 0
change			
equilibrium			

What is the pH of a buffer that is 0.100 M $HC_2H_3O_2$ and 0.100 M $NaC_2H_3O_2$?

K_a for $HC_2H_3O_2 = 1.8 \times 10^{-5}$

$H_2O + HC_2H_3O_2 \Leftrightarrow C_2H_3O_2^- + H_3O^+$

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.100	0.100	0
change	$-x$	$+x$	$+x$
equilibrium	$0.100 - x$	$0.100 + x$	x

represent the change in the concentrations in terms of x

sum the columns to find the equilibrium concentrations in terms of x

substitute into the equilibrium constant expression

$$K_a = \frac{[C_2H_3O_2^-][H_3O^+]}{[HC_2H_3O_2]} = \frac{(0.100 + x)(x)}{(0.100 - x)}$$

What is the pH of a buffer that is 0.100 M $HC_2H_3O_2$ and 0.100 M $NaC_2H_3O_2$?

K_a for $HC_2H_3O_2 = 1.8 \times 10^{-5}$

determine the value of K_a

since K_a is very small, approximate the $[HA]_{eq} = [HA]_{init}$ and $[A^-]_{eq} = [A^-]_{init}$ solve for x

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.100	0.100	≈ 0
change	$0.100 - x$	0.100 $+x$	$+x$
equilibrium	$0.100 - x$	0.100 $+x$	x

$$K_a = \frac{[C_2H_3O_2^-][H_3O^+]}{[HC_2H_3O_2]} = \frac{(0.100+x)(x)}{(0.100-x)}$$

$$K_a = \frac{[C_2H_3O_2^-][H_3O^+]}{[HC_2H_3O_2]} = \frac{(0.100)(x)}{(0.100)}$$

$$1.8 \times 10^{-5} = x$$

What is the pH of a buffer that is 0.100 M $HC_2H_3O_2$ and 0.100 M $NaC_2H_3O_2$?

K_a for $HC_2H_3O_2 = 1.8 \times 10^{-5}$

check if the approximation is valid by seeing if $x <$ 5% of $[HC_2H_3O_2]_{init}$

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.100	0.100	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.100	0.100	x

$x = 1.8 \times 10^{-5}$

$$\frac{1.8\times10^{-5}}{1.00\times10^{-1}}\times100\% = 0.018\% < 5\%$$

the approximation is valid

What is the pH of a buffer that is 0.100 M $HC_2H_3O_2$ and 0.100 M $NaC_2H_3O_2$?

K_a for $HC_2H_3O_2 = 1.8 \times 10^{-5}$

substitute x into the equilibrium concentration definitions and solve

	[HA]	[A^-]	[H_3O^+]
initial	0.100	0.100	≈ 0
change	0.100 - x	0.100 + x	x
equilibrium	0.100	0.100	1.8E-5

$x = 1.8 \times 10^{-5}$

$$\left[HC_2H_3O_2\right] = 0.100 - x = 0.100 - \left(1.8 \times 10^{-5}\right) = 0.100\ M$$

$$\left[C_2H_3O_2^-\right] = 0.100 + x = 0.100 + \left(1.8 \times 10^{-5}\right) = 0.100\ M$$

$$\left[H_3O^+\right] = x = 1.8 \times 10^{-5}\ M$$

What is the pH of a buffer that is 0.100 M $HC_2H_3O_2$ and 0.100 M $NaC_2H_3O_2$?

K_a for $HC_2H_3O_2 = 1.8 \times 10^{-5}$

substitute $[H_3O^+]$ into the formula for pH and solve

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.100	0.100	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.100	0.100	1.8E-5

$$pH = -\log\left(H_3O^+\right)$$

$$= -\log\left(1.8\times10^{-5}\right) = 4.74$$

What is the pH of a buffer that is 0.100 M $HC_2H_3O_2$ and 0.100 M $NaC_2H_3O_2$?

K_a for $HC_2H_3O_2 = 1.8 \times 10^{-5}$

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.100	0.100	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.100	0.100	1.8E-5

check by substituting the equilibrium concentrations back into the equilibrium constant expression and comparing the calculated K_a to the given K_a the values match

$$K_a = \frac{[C_2H_3O_2^-][H_3O^+]}{[HC_2H_3O_2]}$$

$$= \frac{(0.100)(1.8\times10^{-5})}{(0.100)} = 1.8\times10^{-5}$$

What is the pH of a buffer that is 0.14 M HF (pK_a = 3.15) and 0.071 M KF?

K_a for HF = 7.0×10^{-4}

Write the reaction for the acid with water
Construct an ICE table for the reaction
Enter the initial concentrations – assuming the $[H_3O^+]$ from water is ≈ 0

$$H_2O + HF \Leftrightarrow F^- + H_3O^+$$

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.14	0.071	≈ 0
change			
equilibrium			

What is the pH of a buffer that is 0.14 M HF (pK_a = 3.15) and 0.071 M KF?

K_a for HF = 7.0×10^{-4}

$H_2O + HF \Leftrightarrow F^- + H_3O^+$

	[HA]	[A^-]	[H_3O^+]
represent the change in the concentrations in terms of x			
initial	0.14	0.071	0
change	$-x$	$+x$	$+x$
sum the columns to find the equilibrium concentrations in terms of x	0.14 $-x$	0.071 $+ x$	x
substitute into the equilibrium constant expression			

$$K_a = \frac{[F^-][H_3O^+]}{[HF]} = \frac{(0.071 + x)(x)}{(0.14 - x)}$$

What is the pH of a buffer that is 0.14 M HF (pK_a = 3.15) and 0.071 M KF?

K_a for HF = 7.0×10^{-4}

determine the value of K_a
since K_a is very small, approximate the $[HA]_{init}$ and $[A^-]_{init}$ as $[HA]_{eq}$ and $[A^-]_{eq}$

$K_a = 10^{-pK_a}$ solve for x

$K_a = 10^{-3.15} = 7.0 \times 10^{-4}$

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.14	0.071	≈ 0
change	$0.14 - x$	$0.071 + x$	$+x$
equilibrium	0.012	0.083	0.012

$$K_a = \frac{[F^-][H_3O^+]}{[HF]} = \frac{(0.071 + x)(x)}{(0.14 - x)}$$

$$K_a = 7.0 \times 10^{-4} = \frac{(0.071)(x)}{(0.14)}$$

$$1.4 \times 10^{-3} = x$$

What is the pH of a buffer that is 0.14 M HF ($pK_a = 3.15$) and 0.071 M KF?

K_a for HF = 7.0×10^{-4}

check if the approximation is valid by seeing if $x <$ 5% of $[HC_2H_3O_2]_{init}$

	[HA]	$[A_2^-]$	$[H_3O^+]$
initial	0.14	0.071	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.14	0.071	x

$x = 1.4 \times 10^{-3}$

$$\frac{1.4\times10^{-3}}{1.4\times10^{-1}}\times100\% = 1\% < 5\%$$

the approximation is valid

What is the pH of a buffer that is 0.14 M HF (pK_a = 3.15) and 0.071 M KF?

K_a for HF = 7.0×10^{-4}

substitute x into the equilibrium concentration definitions and solve

	[HA]	[A_2^-]	[H_3O^+]
initial	0.14	0.071	≈ 0
change	0.14 -x	0.071 + x	x
equilibrium	0.14	0.072	1.4E-3

$x = 1.4 \times 10^{-3}$

$$[HF] = 0.14 - x = 0.14 - (1.4 \times 10^{-3}) = 0.14\,M$$

$$[C_2H_3O_2^-] = 0.071 + x = 0.071 + (1.4 \times 10^{-3}) = 0.072\,M$$

$$[H_3O^+] = x = 1.4 \times 10^{-3}\,M$$

What is the pH of a buffer that is 0.14 M HF (pK_a = 3.15) and 0.071 M KF?

K_a for HF = 7.0 x 10^{-4}

substitute $[H_3O^+]$ into the formula for pH and solve

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.14	0.071	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.14	0.072	1.4E-3

$$pH = -\log\left(H_3O^+\right)$$

$$= -\log\left(1.4\times10^{-3}\right) = 2.85$$

What is the pH of a buffer that is 0.14 M HF (pK_a = 3.15) and 0.071 M KF?

K_a for HF = 7.0 x 10^{-4}

	[HA]	[A^-]	[H_3O^+]
initial	0.14	0.071	≈ 0
change	-x	+x	+x
equilibrium	0.14	0.072	1.4E-3

$$K_a = \frac{[F^-][H_3O^+]}{[HF]}$$

$$= \frac{(0.072)(1.4\times10^{-3})}{(0.14)} = 7.2\times10^{-4}$$

check by substituting the equilibrium concentrations back into the equilibrium constant expression and comparing the calculated K_a to the given K_a

the values are close enough

Henderson-Hasselbalch Equation

- calculating the pH of a buffer solution can be simplified by using an equation derived from the K_a expression called the **Henderson-Hasselbalch Equation**
- the equation calculates the pH of a buffer from the K_a and initial concentrations of the weak acid and salt of the conjugate base
  - ✓as long as the "*x* is small" approximation is valid

$$pH = pK_a + \log \frac{[\text{conjugate base anion}]_{\text{initial}}}{[\text{weak acid}]_{\text{initial}}}$$

Deriving the Henderson-Hasselbalch Equation

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

$$[H_3O^+] = K_a\left(\frac{[HA]}{[A^-]}\right)$$

Take the log of both sides and multiply by -1

$$-\log[H_3O^+] = -\log\left(K_a\left(\frac{[HA]}{[A^-]}\right)\right)$$

$$-\log[H_3O^+] = -\log K_a + \left(-\log\left(\frac{[HA]}{[A^-]}\right)\right)$$

$$pH = -\log[H_3O^+]$$

$$pH = -\log K_a + \left(-\log\left(\frac{[HA]}{[A^-]}\right)\right)$$

$$pK_a = -\log K_a$$

$$pH = pK_a + \left(-\log\left(\frac{[HA]}{[A^-]}\right)\right)$$

Remember:

$$-\log\frac{[HA]}{[A^-]} = \log\frac{[A^-]}{[HA]}$$

Therefore

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

What is the pH of a buffer that is 0.050 M $HC_7H_5O_2$ and 0.150 M $NaC_7H_5O_2$?

Assume the [HA] and [A^-] equilibrium concentrations are the same as the initial
Substitute into the Henderson-Hasselbalch Equation
Check the "x is small" approximation

$$HC_7H_5O_2 + H_2O \Leftrightarrow C_7H_5O_2^- + H_3O^+$$

K_a for $HC_7H_5O_2 = 6.5 \times 10^{-5}$

$$pK_a = -\log(K_a)$$

$$= -\log(6.5\times10^{-5}) = 4.187$$

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$pH = 4.187 + \log\left(\frac{(0.150)}{0.050}\right)$$

$$pH = 4.66$$

$$[H_3O^+] = 10^{-pH}$$

$$[H_3O^+] = 10^{-4.66} = 2.2\times10^{-5}$$

$$\frac{2.2\times10^{-5}}{0.050}\times100\% = 0.044\%$$

which is < 5%

What is the pH of a buffer that is 0.14 M HF ($pK_a = 3.15$) and 0.071 M KF?

find the pK_a from the given K_a
Assume the [HA] and $[A^-]$ equilibrium concentrations are the same as the initial
Substitute into the Henderson-Hasselbalch Equation
Check the "x is small"

$$HF + H_2O \Leftrightarrow F^- + H_3O^+$$

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$pH = 3.15 + \log\left(\frac{(0.071)}{0.14}\right) = 2.86$$

$$[H_3O^+] = 10^{-pH}$$

$$[H_3O^+] = 10^{-2.86} = 1.4 \times 10^{-3}$$

$$\frac{1.4 \times 10^{-3}}{0.14} \times 100\% = 1\% < 5\%$$

Do I Use the Full Equilibrium Analysis or the Henderson-Hasselbalch Equation?

- the Henderson-Hasselbalch equation is generally good enough when the "*x* is small" approximation is applicable
- generally, the "*x* is small" approximation will work when both of the following are true:

a) the initial concentrations of acid and salt are not very dilute

b) the K_a is fairly small

- for most problems, this means that the initial acid and salt concentrations should be over 1000x larger than the value of K_a

How Much Does the pH of a Buffer Change When an Acid or Base Is Added?

- although buffers do resist change in pH when acid or base are added to them, their pH does change
- calculating the new pH after adding acid or base requires breaking the problem into 2 parts

1. a stoichiometry calculation for the reaction of the added chemical with one of the ingredients of the buffer to reduce its initial concentration and increase the concentration of the other
   - ✓ added acid reacts with the A^- to make more HA
   - ✓ added base reacts with the HA to make more A^-
2. an equilibrium calculation of $[H_3O^+]$ using the new initial values of [HA] and $[A^-]$

What is the pH of a buffer that has 0.100 mol $HC_2H_3O_2$ and 0.100 mol $NaC_2H_3O_2$ in 1.00 L that has 0.010 mol NaOH added to it?

If the added chemical is a base, write a reaction for OH^- with HA. If the added chemical is an acid, write a reaction for it with A^-.

$$HC_2H_3O_2 + OH^- \Leftrightarrow C_2H_3O_2^- + H_2O$$

Construct a stoichiometry table for the reaction

	HA	A^-	OH^-
mols Before	0.100	0.100	0
mols added	-	-	0.010
mols After			

What is the pH of a buffer that has 0.100 mol $HC_2H_3O_2$ and 0.100 mol $NaC_2H_3O_2$ in 1.00 L that has 0.010 mol NaOH added to it?

$$HC_2H_3O_2 + OH^- \Leftrightarrow C_2H_3O_2^- + H_2O$$

Fill in the table – tracking the changes in the number of moles for each component

	HA	A^-	OH^-
mols Before	0.100	0.100	≈ 0
mols added	-	-	0.010
mols After	0.090	0.110	≈ 0

What is the pH of a buffer that has 0.100 mol $HC_2H_3O_2$ and 0.100 mol $NaC_2H_3O_2$ in 1.00 L that has 0.010 mol NaOH added to it?

Write the reaction for the acid with water
Construct an ICE table for the reaction
Enter the initial concentrations – assuming the $[H_3O^+]$ from water is ≈ 0, and using the new molarities of the [HA] and

$$HC_2H_3O_2 + H_2O \Leftrightarrow C_2H_3O_2^- + H_3O^+$$

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.090	0.110	≈ 0
change			
equilibrium			

What is the pH of a buffer that has 0.100 mol $HC_2H_3O_2$ and 0.100 mol $NaC_2H_3O_2$ in 1.00 L that has 0.010 mol NaOH added to it?

$$HC_2H_3O_2 + H_2O \Leftrightarrow C_2H_3O_2^- + H_3O^+$$

represent the change in the concentrations in terms of *x*	
sum the columns to find the equilibrium concentrations in terms of *x*	
substitute into the equilibrium constant expression	

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.090	0.110	0
change	$-x$	$+x$	$+x$
equilibrium	$0.090 - x$	$0.110 + x$	x

$$K_a = \frac{[C_2H_3O_2^-][H_3O^+]}{[HC_2H_3O_2]} = \frac{(0.110 + x)(x)}{(0.090 - x)}$$

What is the pH of a buffer that has 0.100 mol $HC_2H_3O_2$ and 0.100 mol $NaC_2H_3O_2$ in 1.00 L that has 0.010 mol NaOH added to it?

K_a for $HC_2H_3O_2 = 1.8 \times 10^{-5}$

determine the value of K_a

since K_a is very small, approximate the $[HA]_{eq} = [HA]_{init}$ and $[A^-]_{eq} = [A^-]_{init}$ solve for x

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.100	0.100	≈ 0
change	0.090	0.110	$+x$
equilibrium	$-x$ ~~$\approx$~~ 0.090	$+x$ ~~$\approx$~~ 0.110	x

$$K_a = \frac{[C_2H_3O_2^-][H_3O^+]}{[HC_2H_3O_2]} = \frac{(0.110)(x)}{(0.090)}$$

$$1.8\times10^{-5} = \frac{(0.110)(x)}{(0.090)}$$

$$1.47\times10^{-5} = x$$

What is the pH of a buffer that has 0.100 mol $HC_2H_3O_2$ and 0.100 mol $NaC_2H_3O_2$ in 1.00 L that has 0.010 mol NaOH added to it?

K_a for $HC_2H_3O_2 = 1.8 \times 10^{-5}$

check if the approximation is valid by seeing if $x <$ 5% of $[HC_2H_3O_2]_{init}$

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.090	0.110	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	$0.090 - x$	0.110	x

$x = 1.47 \times 10^{-5}$

$$\frac{1.47\times10^{-5}}{9.0\times10^{-2}}\times100\% = 0.016\% < 5\%$$

the approximation is valid

What is the pH of a buffer that has 0.100 mol $HC_2H_3O_2$ and 0.100 mol $NaC_2H_3O_2$ in 1.00 L that has 0.010 mol NaOH added to it?

substitute x into the equilibrium concentration definitions and solve

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.090	0.110	≈ 0
change	$0.090 - x$	$0.110 + x$	x
equilibrium	0.090	0.110	1.5E-5

$x = 1.47 \times 10^{-5}$

$$\left[HC_2H_3O_2\right] = 0.090 - x = 0.090 - \left(1.47 \times 10^{-5}\right) = 0.090\ \text{M}$$

$$\left[C_2H_3O_2^-\right] = 0.110 + x = 0.110 + \left(1.47 \times 10^{-5}\right) = 0.110\ \text{M}$$

$$\left[H_3O^+\right] = x = 1.47 \times 10^{-5}\ \text{M}$$

What is the pH of a buffer that has 0.100 mol $HC_2H_3O_2$ and 0.100 mol $NaC_2H_3O_2$ in 1.00 L that has 0.010 mol NaOH added to it?

substitute $[H_3O^+]$ into the formula for pH and solve

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.090	0.110	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.090	0.110	1.5E-5

$$pH = -\log\left(H_3O^+\right)$$

$$= -\log\left(1.47\times10^{-5}\right) = 4.83$$

What is the pH of a buffer that has 0.100 mol $HC_2H_3O_2$ and 0.100 mol $NaC_2H_3O_2$ in 1.00 L that has 0.010 mol NaOH added to it?

K_a for $HC_2H_3O_2 = 1.8 \times 10^{-5}$

	[HA]	$[A^-]$	$[H_3O^+]$
initial	0.090	0.110	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.090	0.110	1.5E-5

$$K_a = \frac{[C_2H_3O_2^-][H_3O^+]}{[HC_2H_3O_2]}$$

$$= \frac{(0.110)(1.47\times10^{-5})}{(0.090)} = 1.8\times10^{-5}$$

check by substituting the equilibrium concentrations back into the equilibrium constant expression and comparing the calculated K_a to the given K_a the values match

What is the pH of a buffer that has 0.100 mol $HC_2H_3O_2$ and 0.100 mol $NaC_2H_3O_2$ in 1.00 L that has 0.010 mol NaOH added to it?

find the pK_a from the given K_a
Assume the [HA] and [A^-] equilibrium concentrations are the same as the initial

$$HC_2H_3O_2 + H_2O \Leftrightarrow C_2H_3O_2^- + H_3O^+$$

K_a for $HC_2H_3O_2 = 1.8 \times 10^{-5}$

$$pK_a = -\log K_a$$

$$= -\log\left(1.8\times10^{-5}\right)$$

$$= 4.745$$

	[HA]	[A^-]	[H_3O^+]
initial	0.090	0.110	≈ 0
change	$-x$	$+x$	$+x$
equilibrium	0.090	0.110	x

What is the pH of a buffer that has 0.100 mol $HC_2H_3O_2$ and 0.100 mol $NaC_2H_3O_2$ in 1.00 L that has 0.010 mol NaOH added to it?

Substitute into the Henderson-Hasselbalch Equation
Check the "x is small" approximation

$$HC_2H_3O_2 + H_2O \Leftrightarrow C_2H_3O_2^- + H_3O^+$$

$$pK_a \text{ for } HC_2H_3O_2 = 4.745$$

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$pH = 4.745 + \log\left(\frac{(0.110)}{0.090}\right) = 4.833$$

$$[H_3O^+] = 10^{-pH}$$

$$[H_3O^+] = 10^{-4.83} = 1.47 \times 10^{-5}$$

$$\frac{1.47 \times 10^{-5}}{0.090} \times 100\% = 0.016\% < 5\%$$

Compare the effect on pH of adding 0.010 mol NaOH to a buffer that has 0.100 mol $HC_2H_3O_2$ and 0.100 mol $NaC_2H_3O_2$ in 1.00 L to adding 0.010 mol NaOH to 1.00 L of pure water?

$$HC_2H_3O_2 + H_2O \Leftrightarrow C_2H_3O_2^- + H_3O^+$$

pK_a for $HC_2H_3O_2 = 4.745$

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$pH = 4.745 + \log\left(\frac{(0.110)}{0.090}\right)$$

$$= 4.83$$

$$[OH^-] = \frac{0.010\ mol}{1.00\ L} = 0.010\ M$$

$$pOH = -\log[OH^-]$$

$$= -\log\left(1.0\times10^{-2}\right) = 2.00$$

$$pH + pOH = 14.00$$

$$pH = 14.00 - pOH$$

$$= 14.00 - 2.00$$

$$= 12.00$$

What is the pH of a buffer that is 0.50 M NH_3 ($pK_b = 4.75$) and 0.20 M NH_4Cl?

find the pK_a of the conjugate acid (NH_4^+) from the given K_b
Assume the [B] and [HB^+] equilibrium concentrations are the same as the initial
Substitute into the Henderson-Hasselbalch Equation

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$$

$$pK_a + pK_b = 14$$

$$pK_a = 14 - pK_b = 14 - 4.75 = 9.25$$

$$pH = pK_a + \log\left(\frac{[B]}{[HB^+]}\right)$$

$$pH = 9.25 + \log\left(\frac{(0.50)}{(0.20)}\right) = 9.65$$

$$[H_3O^+] = 10^{-pH}$$

$$[H_3O^+] = 10^{-9.65} = 2.23 \times 10^{-10}$$

$$\frac{2.23 \times 10^{-10}}{0.20} \times 100\% <<< 5\%$$

Buffering Effectiveness

- a good buffer should be able to neutralize moderate amounts of added acid or base
- however, there is a limit to how much can be added before the pH changes significantly
- the **buffering capacity** is the amount of acid or base a buffer can neutralize
- the **buffering range** is the pH range the buffer can be effective
- the effectiveness of a buffer depends on two factors (1) the relative amounts of acid and base, and (2) the absolute concentrations of acid and base

Effect of Relative Amounts of Acid & Conjugate Base

Buffers are most effective when [acid] = [base]

Buffer 1

0.100 mol HA & 0.100 mol A^-

Initial pH = 5.00

$HA + OH^- \Leftrightarrow A^- + H_2O$

	HA	A^-	OH^-
mols Before	0.100	0.100	0
mols added	-	-	0.010
mols After	0.090	0.110	≈ 0

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

pK_a (HA) = 5.00

$$pH = 5.00 + \log\left(\frac{(0.110)}{0.090}\right) = 5.09$$

Effect of Relative Amounts of Acid & Conjugate Base

Buffers are most effective when [acid] = [base]

Buffer 12

0.18 mol HA & 0.020 mol A^-

Initial pH = 4.05

	HA	A^-	OH^-
mols Before	0.18	0.020	0
mols added	-	-	0.010
mols After	0.17	0.030	≈ 0

$$HA + OH^- \Leftrightarrow A^- + H_2O$$

$$pK_a\ (HA) = 5.00$$

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$pH = 5.00 + \log\left(\frac{(0.030)}{0.17}\right) = 4.25$$

Effect of Relative Amounts of Acid and Conjugate Base

Buffers are most effective when [acid] = [base]

Buffer 1

0.100 mol HA & 0.100 mol A^-
Initial pH = 5.00

pK_a (HA) = 5.00

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$HA + OH^- \Leftrightarrow A^- + H_2O$$

after adding 0.010 mol NaOH
pH = 5.09

$$pH = 5.00 + \log\left(\frac{(0.110)}{0.090}\right) = 5.09$$

	HA	A^-	OH^-
mols Before	0.100	0.100	0
mols added	-	-	0.010

$$\%\,\text{Change} = \frac{(5.09 - 5.00)}{5.00} \times 100\% = 1.8\%$$

Effect of Relative Amounts of Acid and Conjugate Base

Buffers are most effective when [acid] = [base]

Buffer 1 = Buffer 2

0.18 mol HA & 0.020 mol A^-

Initial pH = 4.05

pK_a (HA) = 5.00

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

$HA + OH^- \Leftrightarrow A^- + H_2O$

	HA	A^-	OH^-
mols Before	0.18	0.020	0
mols added	-	-	0.010
		0.030	

after adding 0.010 mol NaOH

$$pH = 5.00 + \log\left(\frac{(0.030)}{0.17}\right) = 4.25$$

after adding 0.010 mol NaOH

pH = 4.25

% Change

$$= \frac{(4.25 - 4.05)}{4.05} \times 100\%$$

$= 5.0\%$

Start: Effect of Absolute Concentrations of Acid and Conjugate Base

a buffer is most effective when the concentrations of acid and base are largest (0.1M vs. 0.5M)

Buffer 1:

.50 mol HA & 0.50 mol A^-

Initial pH = 5.00

pK_a (HA) = 5.00

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$HA + OH^- \Leftrightarrow A^- + H_2O$$

fter adding 0.010 mol NaOH

pH = 5.02

$$pH = 5.00 + \log\left(\frac{(0.51)}{0.49}\right) = 5.02$$

	HA	A^-	OH^-
mols Before	0.50	0.50 0	0
mols added	-	-	0.01 0

$$\%\,\text{Change} = \frac{(5.02 - 5.00)}{5.00} \times 100\% = 0.4\%$$

vs. 5.09 for 0.1M

vs. 1.8% for 0.1M

Effect of Absolute Concentrations of Acid and Conjugate Base

a buffer is most effective when the concentrations of acid and base are largest

Buffer 12

0.050 mol HA & 0.050 mol A^-

Initial pH = 5.00

pK_a (HA) = 5.00

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$HA + OH^- \Leftrightarrow A^- + H_2O$$

after adding 0.010 mol NaOH

pH = 5.18

Add 0.01 mol NaOH

$$pH = 5.00 + \log\left(\frac{(0.060)}{0.040}\right) = 5.18$$

	HA	A^-	OH^-
mols Before	0.050	0.050	0
mols added	-	-	0.010

$$\%\,\text{Change} = \frac{(5.18 - 5.00)}{5.00} \times 100\% = 3.6\%$$

Effectiveness of Buffers

- a buffer will be most effective when the [base]:[acid] = 1
  - ✓equal concentrations of acid and base
- effective when 0.1 < [base]:[acid] < 10
- a buffer will be most effective when the [acid] and the [base] are large

Buffering Range

- we have said that a buffer will be effective when

$$0.1 < [\text{base}]:[\text{acid}] < 10$$

- substituting into the Henderson-Hasselbalch we can calculate the maximum and minimum pH at which the buffer will be effective

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

Lowest pH

$$pH = pK_a + \log(0.10)$$

$$pH = pK_a - 1$$

Highest pH

$$pH = pK_a + \log(10)$$

$$pH = pK_a + 1$$

Therefore, the effective pH range of a buffer is $pK_a \pm 1$

when choosing an acid to make a buffer, choose one whose is pK_a is closest to the pH of the buffer

Which of the following acids would be the best choice to combine with its sodium salt to make a buffer with pH 4.25?

Chlorous Acid, $HClO_2$	$pK_a = 1.95$
Nitrous Acid, HNO_2	$pK_a = 3.34$
Formic Acid, $HCHO_2$	$pK_a = 3.74$
Hypochlorous Acid, $HClO$	$pK_a = 7.54$

Which of the following acids would be the best choice to combine with its sodium salt to make a buffer with pH 4.25?

Chlorous Acid, $HClO_2$	$pK_a = 1.95$
Nitrous Acid, HNO_2	$pK_a = 3.34$
Formic Acid, $HCHO_2$	$pK_a = 3.74$
Hypochlorous Acid, $HClO$	$pK_a = 7.54$

The pK_a of $HCHO_2$ is closest to the desired pH of the buffer, so it would give the most effective buffering range.

What ratio of $NaCHO_2$: $HCHO_2$ would be required to make a buffer with pH 4.25?

Formic Acid, $HCHO_2$, $pK_a = 3.74$

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$4.25 = 3.74 + \log\left(\frac{[CHO_2^-]}{[HCHO_2]}\right)$$

$$0.51 = \log\left(\frac{[CHO_2^-]}{[HCHO_2]}\right)$$

$$10^{\log\left(\frac{[CHO_2^-]}{[HCHO_2]}\right)} = 10^{0.51}$$

$$\frac{[CHO_2^-]}{[HCHO_2]} = 3.24$$

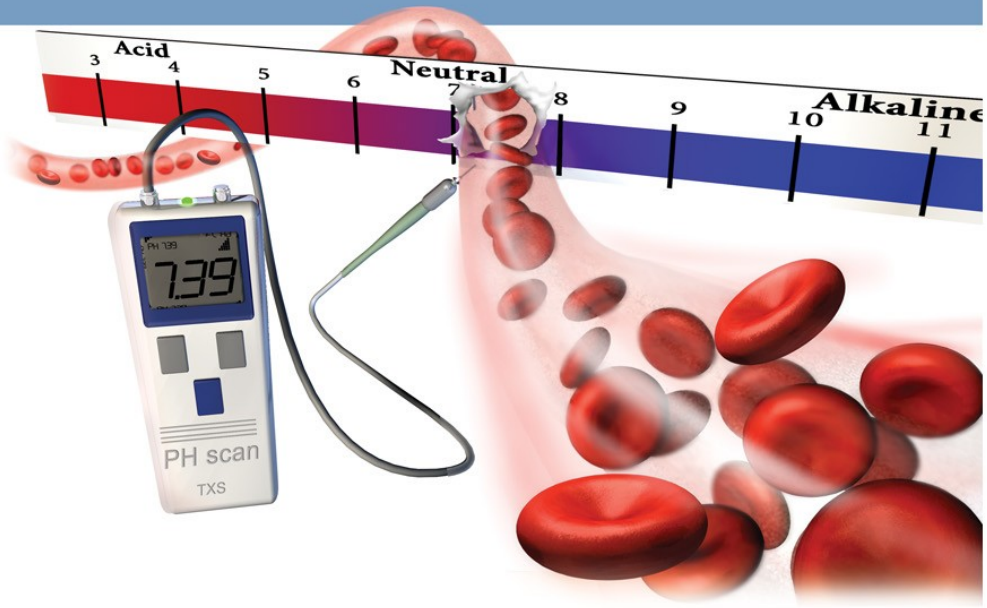
to make the buffer with pH 4.25, you would use 3.24 times as much $NaCHO_2$ as $HCHO_2$

Buffering Capacity

- buffering capacity is the amount of acid or base that can be added to a buffer without destroying its effectiveness
- the buffering capacity increases with increasing absolute concentration of the buffer components
- as the [base]:[acid] ratio approaches 1, the ability of the buffer to neutralize both added acid and base improves
- buffers that need to work mainly with added acid generally have [base] > [acid]
- buffers that need to work mainly with added base generally have [acid] > [base]

Chapter 15: Applications of Aqueous Equilibria - Solubility Equilibria

GENERAL CHEMISTRY: ATOMS FIRST



John E. McMurray – Robert C. Fay

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Solubility Equilibria

- all ionic compounds dissolve in water to some degree
  - ✓ however, many compounds have such low solubility in water that we classify them as insoluble
- we can apply the concepts of equilibrium to salts dissolving, and use the equilibrium constant for the process to measure relative solubilities in water

Solubility Product

- the equilibrium constant for the dissociation of a solid salt into its aqueous ions is called the **solubility product, K_{sp}**
- for an ionic solid M_nX_m, the dissociation reaction is:

$$M_nX_m(s) \Leftrightarrow nM^{m+}(aq) + mX^{n-}(aq)$$

- the solubility product would be

$$K_{sp} = [M^{m+}]^n[X^{n-}]^m$$

- for example, the dissociation reaction for $PbCl_2$ is

$$PbCl_2(s) \Leftrightarrow Pb^{2+}(aq) + 2\ Cl^-(aq)$$

- and its equilibrium constant is

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

TABLE 16.2 Selected Solubility Product Constants (K_{sp})

Compound	Formula	K_{sp}	Compound	Formula	K_{sp}
Barium fluoride	BaF_2	2.45×10^{-5}	Lead(II) chloride	$PbCl_2$	1.17×10^{-5}
Barium sulfate	$BaSO_4$	1.07×10^{-10}	Lead(II) bromide	$PbBr_2$	4.67×10^{-6}
Calcium carbonate	$CaCO_3$	4.96×10^{-9}	Lead(II) sulfate	$PbSO_4$	1.82×10^{-8}
Calcium fluoride	CaF_2	1.46×10^{-10}	Lead(II) sulfide	PbS	9.04×10^{-29}
Calcium hydroxide	$Ca(OH)_2$	4.68×10^{-6}	Magnesium carbonate	$MgCO_3$	6.82×10^{-6}
Calcium sulfate	$CaSO_4$	7.10×10^{-5}	Magnesium hydroxide	$Mg(OH)_2$	2.06×10^{-13}
Copper(II) sulfide	CuS	1.27×10^{-36}	Silver chloride	AgCl	1.77×10^{-10}
Iron(II) carbonate	$FeCO_3$	3.07×10^{-11}	Silver chromate	Ag_2CrO_4	1.12×10^{-12}
Iron(II) hydroxide	$Fe(OH)_2$	4.87×10^{-17}	Silver bromide	AgBr	5.35×10^{-13}
Iron(II) sulfide	FeS	3.72×10^{-19}	Silver iodide	AgI	8.51×10^{-17}

Molar Solubility

- solubility is the amount of solute that will dissolve in a given amount of solution
  - ✓ at a particular temperature
- the **molar solubility** is the number of moles of solute that will dissolve in a liter of solution
  - ✓ the molarity of the dissolved solute in a saturated solution
- for the general reaction $M_nX_m(s) \Leftrightarrow nM^{m+}(aq) + mX^{n-}(aq)$

$$\text{molar solubility} = s = \sqrt[(n+m)]{\frac{K_{sp}}{n^n \cdot m^m}}$$

Ex 16.8 – Calculate the molar solubility of $PbCl_2$ in pure water at 25°C

Write the dissociation reaction and K_{sp} expression

$$PbCl_2(s) \Leftrightarrow Pb^{2+}(aq) + 2\ Cl^-(aq)$$

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

Create an ICE table defining the change in terms of the solubility of the solid

	$[Pb^{2+}]$	$[Cl^-]$
Initial	0	0
Change	+S	+2S
Equilibrium	S	2S

Ex 16.8 – Calculate the molar solubility of $PbCl_2$ in pure water at 25°C

Substitute into the K_{sp} expression

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

$$K_{sp} = (S)(2S)^2$$

Find the value of K_{sp} from Table 16.2, plug into the equation and solve for S

	Pb^{2+}	Cl^-
Initial	0	0
Change	+S	+2S
Equilibrium	S	2S

$$K_{sp} = 4S^3$$

$$S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.17\times10^{-5}}{4}}$$

$$S = 1.43\times10^{-2}\ M$$

Practice – Determine the K_{sp} of $PbBr_2$ if its molar solubility in water at 25°C is 1.05×10^{-2} M

Practice – Determine the K_{sp} of $PbBr_2$ if its molar solubility in water at 25°C is 1.05×10^{-2} M

Write the dissociation reaction and K_{sp} expression

$$PbBr_2(s) \Leftrightarrow Pb^{2+}(aq) + 2\ Br^{-}(aq)$$

$$K_{sp} = [Pb^{2+}][Br^{-}]^2$$

Create an ICE table defining the change in terms of the solubility of the solid

	$[Pb^{2+}]$	$[Br^{-}]$
Initial	0	0
Change	$+(1.05 \times 10^{-2})$	$+2(1.05 \times 10^{-2})$
Equilibrium	(1.05×10^{-2})	(2.10×10^{-2})

Practice – Determine the K_{sp} of $PbBr_2$ if its molar solubility in water at 25°C is 1.05×10^{-2} M

Substitute into the K_{sp} expression

$$K_{sp} = [Pb^{2+}][Br^-]^2$$

$$K_{sp} = (1.05 \times 10^{-2})(2.10 \times 10^{-2})^2$$

plug into the equation and solve

	$[Pb^{2+}]$	$[Br^-]$
Initial	0	0
Change	+(1.05 x 10^{-2})	+2(1.05 x 10^{-2})
Equilibrium	(1.05 x 10^{-2})	(2.10 x 10^{-2})

$$K_{sp} = (1.05 \times 10^{-2})(2.10 \times 10^{-2})^2$$

$$K_{sp} = 4.63 \times 10^{-6}$$

K_{sp} and Relative Solubility

- molar solubility is related to K_{sp}
- but you cannot always compare solubilities of compounds by comparing their K_{sp} values
- in order to compare K_{sp} values, the compounds must have the same dissociation stoichiometry

The Effect of Common Ion on Solubility

- addition of a soluble salt that contains one of the ions of the “insoluble” salt, decreases the solubility of the “insoluble” salt
- for example, addition of NaCl to the solubility equilibrium of solid $PbCl_2$ decreases the solubility of $PbCl_2$

$$PbCl_2(s) \Leftrightarrow Pb^{2+}(aq) + 2\ Cl^-(aq)$$

addition of Cl^- shifts the equilibrium to the left

Ex 16.10 – Calculate the molar solubility of CaF_2 in 0.100 M NaF at 25°C

Write the dissociation reaction and K_{sp} expression

$$CaF_2(s) \Leftrightarrow Ca^{2+}(aq) + 2\ F^-(aq)$$

$$K_{sp} = [Ca^{2+}][F^-]^2$$

Create an ICE table defining the change in terms of the solubility of the solid

	$[Ca^{2+}]$	$[F^-]$
Initial	0	0.100
Change	+S	+2S
Equilibrium	S	0.100 + 2S

Ex 16.10 – Calculate the molar solubility of CaF_2 in 0.100 M NaF at 25°C

Substitute into the K_{sp} expression assume S is small

$$K_{sp} = [Ca^{2+}][F^-]^2$$

$$K_{sp} = (S)(0.100 + 2S)^2$$

$$K_{sp} = (S)(0.100)^2$$

Find the value of K_{sp} from Table 16.2, plug into the equation and solve for S

	$[Ca^{2+}]$	$[F^-]$
Initial	0	0.100
Change	+S	+2S
Equilibrium	S	0.100 + 2S

$$K_{sp} = S(0.100)^2$$

$$S = \frac{1.46 \times 10^{-10}}{(0.100)^2}$$

$$S = 1.46 \times 10^{-8}\ M$$

The Effect of pH on Solubility

- for insoluble ionic hydroxides, the higher the pH, the lower the solubility of the ionic hydroxide
  - ✓ and the lower the pH, the higher the solubility
  - ✓ higher pH = increased [OH–]

$$M(OH)_n(s) \Leftrightarrow M^{n+}(aq) + nOH^-(aq)$$

- for insoluble ionic compounds that contain anions of weak acids, the lower the pH, the higher the solubility

$$M_2(CO_3)_n(s) \Leftrightarrow 2\ M^{n+}(aq) + nCO_3^{2-}(aq)$$

$$H_3O^+(aq) + CO_3^{2-}(aq) \Leftrightarrow HCO_3^-(aq) + H_2O(l)$$

Precipitation

- precipitation will occur when the concentrations of the ions exceed the solubility of the ionic compound
- if we compare the reaction quotient, Q, for the current solution concentrations to the value of K_{sp}, we can determine if precipitation will occur
  - ✓ $Q = K_{sp}$, the solution is saturated, no precipitation
  - ✓ $Q < K_{sp}$, the solution is unsaturated, no precipitation
  - ✓ $Q > K_{sp}$, the solution would be above saturation, the salt above saturation will precipitate
- some solutions with $Q > K_{sp}$ will not precipitate unless disturbed – these are called **supersaturated** solutions

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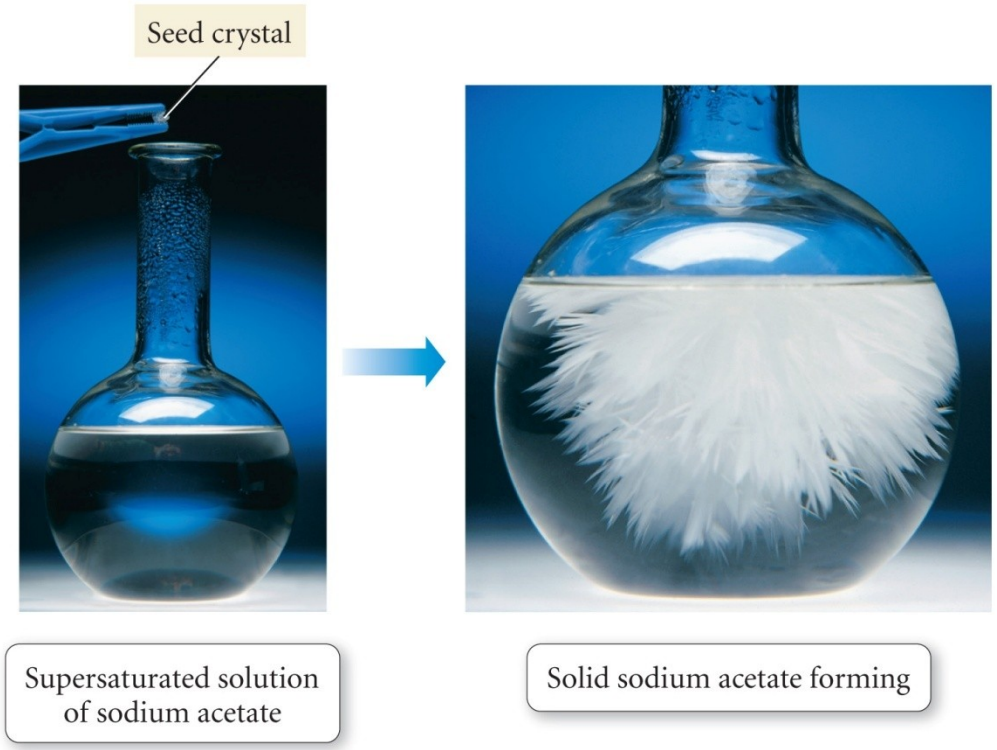

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precipitation occurs if $Q > K_{sp}$

a supersaturated solution will precipitate if a seed crystal is added

Selective Precipitation

- a solution containing several different cations can often be separated by addition of a reagent that will form an insoluble salt with one of the ions, but not the others
- a successful reagent can precipitate with more than one of the cations, as long as their K_{sp} values are significantly different

Ex 16.13 What is the minimum $[OH^-]$ necessary to just begin to precipitate Mg^{2+} (with [0.059]) from seawater?

precipitating may just occur when $Q = K_{sp}$

From the K_{sp} table: $K_{sp} = 2.06 \times 10^{-13}$

$$Q = [Mg^{2+}][OH^-]^2$$

$$Q = K_{sp}$$

$$[(0.059)][OH^-]^2 = 2.06 \times 10^{-13}$$

$$[OH^-] = \sqrt{\frac{(2.06 \times 10^{-13})}{(0.059)}} = 1.9 \times 10^{-6}$$

Ex 16.14 What is the $[Mg^{2+}]$ when Ca^{2+} (with [0.011]) just begins to precipitate from seawater?

cipitating Mg^{2+} begins when $[OH^-] = 1.9 \times 10$

$$Q = [Ca^{2+}][OH^-]^2$$

$$Q = K_{sp}$$

$$[(0.011)][OH^-]^2 = 4.68 \times 10^{-6}$$

$$[OH^-] = \sqrt{\frac{(4.68 \times 10^{-6})}{(0.011)}} = 2.06 \times 10^{-2}$$

Ex 16.14 What is the $[Mg^{2+}]$ when Ca^{2+} (with [0.011]) just begins to precipitate from seawater?

cipitating Mg^{2+} begins when $[OH^-] = 1.9 \times 10$

ipitating Ca^{2+} begins when $[OH^-] = 2.\underline{0}6 \times 10$

$$Q = [Mg^{2+}][OH^-]^2$$

$$\text{when } Q = K_{sp}$$

$$[Mg^{2+}]\left[\left(2.\underline{0}6\times10^{-2}\right)\right]^2 = 2.06\times10^{-13}$$

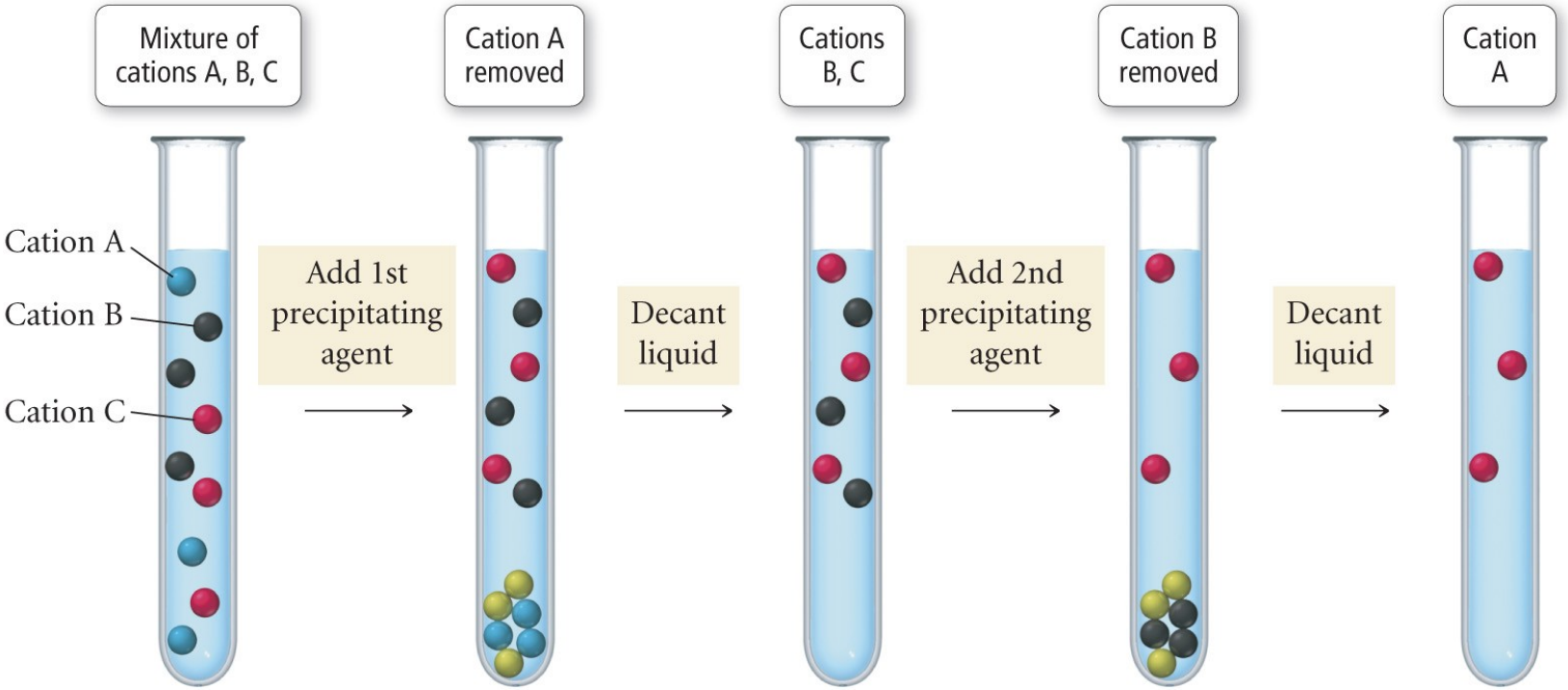
$$[Mg^{2+}] = \frac{\left(2.06\times10^{-13}\right)}{\left(2.\underline{0}6\times10^{-2}\right)^2} = 4.8\times10^{-10}\,\text{M}$$

when Ca^{2+} just begins to precipitate out, the $[Mg^{2+}]$ has dropped from 0.059 M to 4.8 x 10^{-10} M

Qualitative Analysis

- an analytical scheme that utilizes selective precipitation to identify the ions present in a solution is called a **qualitative analysis** scheme
  - ✓wet chemistry
- a sample containing several ions is subjected to the addition of several precipitating agents
- addition of each reagent causes one of the ions present to precipitate out

Qualitative Analysis



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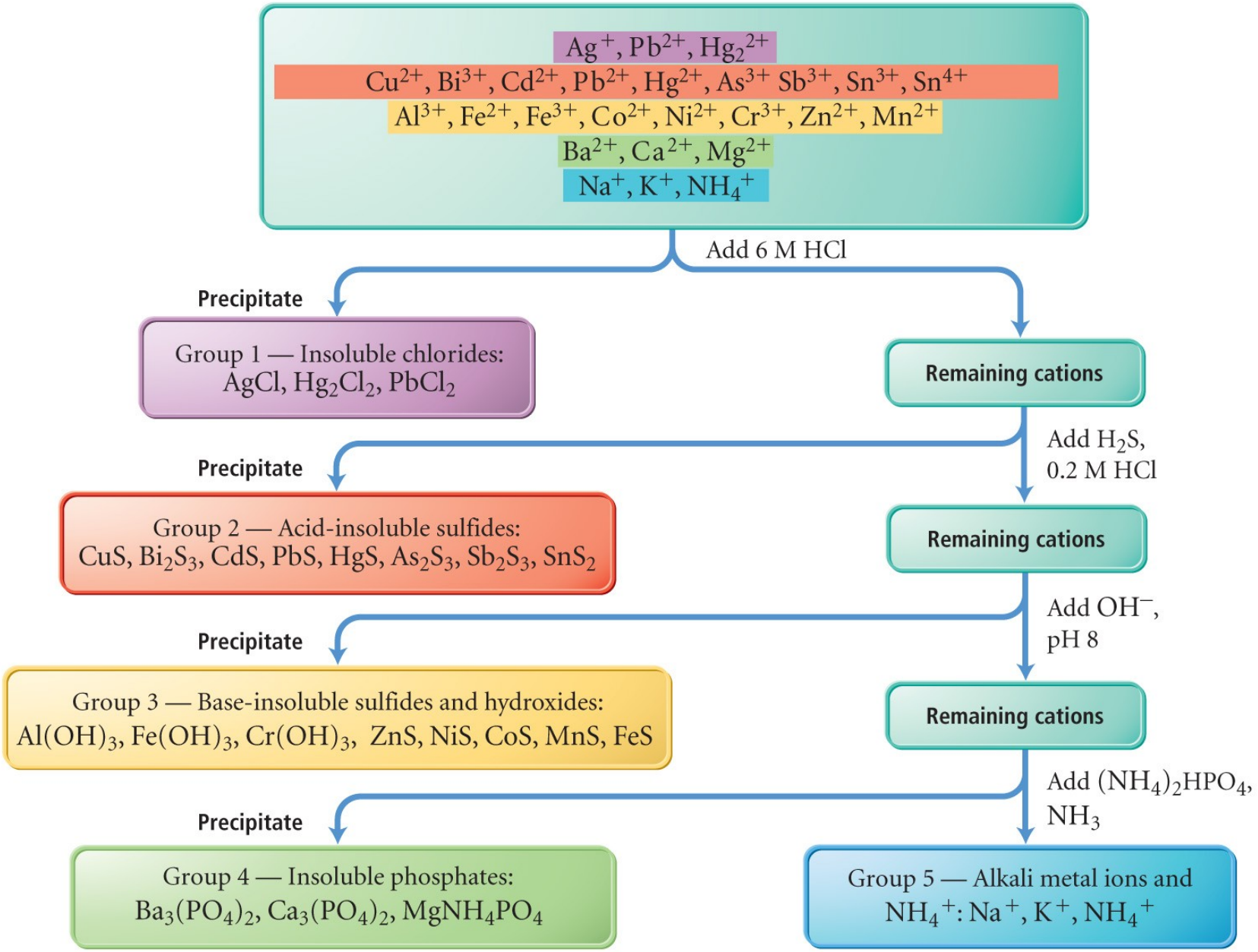
Ag^+, Pb^{2+}, Hg_2^{2+}
Cu^{2+}, Bi^{3+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, As^{3+} Sb^{3+}, Sn^{3+}, Sn^{4+}
Al^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Zn^{2+}, Mn^{2+}
Ba^{2+}, Ca^{2+}, Mg^{2+}
Na^+, K^+, NH_4^+
Add 6 M HCl
Precipitate
Group 1 — Insoluble chlorides:
$AgCl$, Hg_2Cl_2, $PbCl_2$
Remaining cations
Add H_2S, 0.2 M HCl
Precipitate
Group 2 — Acid-insoluble sulfides:
CuS, Bi_2S_3, CdS, PbS, HgS, As_2S_3, Sb_2S_3, SnS_2
Remaining cations
Add OH^-, pH 8
Precipitate
Group 3 — Base-insoluble sulfides and hydroxides:
$Al(OH)_3$, $Fe(OH)_3$, $Cr(OH)_3$, ZnS, NiS, CoS, MnS, FeS
Remaining cations
Add $(NH_4)_2HPO_4$, NH_3
Precipitate
Group 4 — Insoluble phosphates:
$Ba_3(PO_4)_2$, $Ca_3(PO_4)_2$, $MgNH_4PO_4$
Group 5 — Alkali metal ions and NH_4^+: Na^+, K^+, NH_4^+

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Group 1 Insoluble Chlorides

- group one cations are Ag^{+}, Pb^{2+}, and Hg_2^{2+}
- they form water insoluble compounds with Cl^-
  - ✓ $AgCl$, $PbCl_2$, Hg_2Cl_2
  - ✓ as long as the concentration is large enough
  - ✓ $PbCl_2$ may be borderline
    - ➢ molar solubility of $PbCl_2 = 1.43 \times 10^{-2}$ M
- precipitated by the addition of HCl, which acts to decrease the solubility due to LeChatelier's principle.

Group 2 Acid Insoluble Sulfides

- group two cations are Cd^{2+}, Cu^{2+}, Bi^{3+}, Sn^{4+}, As^{3+}, Pb^{2+}, Sb^{3+}, and Hg^{2+}
- HgS, CdS, CuS, SnS_2 ,etc.
- they form water insoluble compounds with HS^- and S^{2-} at low pH
- They are precipitated by the addition of H_2S in HCl

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Group 3 Base Insoluble Sulfides & Hydroxides

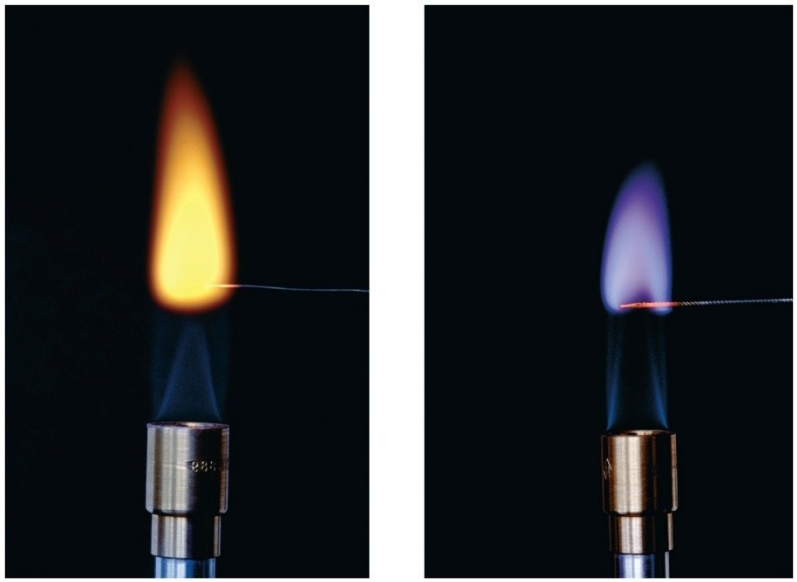
- group three cations are Fe^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+} precipitated as sulfides
  - ✓ FeS, CoS, ZnS, MnS, NiS
- Cr^{3+}, Fe^{3+}, and Al^{3+} precipitated as hydroxides
  - ✓ $Al(OH_3)$, $Fe(OH_3)$, $Cr(OH_3)$
- all these cations form compounds with S^{2-} that are insoluble in water at high pH
- precipitated by the addition of H_2S in NaOH

Group 4 Insoluble Phosphates

- group four cations are Mg^{2+}, Ca^{2+}, Ba^{2+}
- all these cations form compounds with PO_4^{3-} that are insoluble in water at high pH
- precipitated by the addition of $(NH_4)_2HPO_4$

Group 5

- group five cations are Na^+, K^+, NH_4^+
- all these cations form compounds that are soluble in water – they do not precipitate
- They are identified by the color of their flame



Sodium Potassium

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Complex Ion Formation

- transition metals tend to be good Lewis acids
- they often bond to one or more H_2O molecules to form a hydrated ion
  - ✓ H_2O is the Lewis base, donating electron pairs to form coordinate covalent bonds

$$Ag^+(aq) + 2\ H_2O(l) \Leftrightarrow Ag(H_2O)_2^+(aq)$$

- ions that form by combining a cation with several anions or neutral molecules are called **complex ions**
  - ✓ e.g., $Ag(H_2O)_2^+$
- the attached ions or molecules are called **ligands**
  - ✓ e.g., H_2O

Complex Ion Equilibria

- if a ligand is added to a solution and it forms a stronger bond than the original ligand, it will replace the original ligand

$$Ag(H_2O)_2^{+}{}_{(aq)} + 2\ NH_{3(aq)} \Leftrightarrow Ag(NH_3)_2^{+}{}_{(aq)} + 2\ H_2O_{(l)}$$

  - ✓ generally H_2O is not included, since its complex ion is always present in aqueous solution

$$Ag^{+}{}_{(aq)} + 2\ NH_{3(aq)} \Leftrightarrow Ag(NH_3)_2^{+}{}_{(aq)}$$

Formation Constant

- the reaction between an ion and ligands to form a complex ion is called a **complex ion formation reaction**

$$Ag^{+}_{(aq)} + 2\ NH_{3(aq)} \Leftrightarrow Ag(NH_3)_2{}^{+}_{(aq)}$$

- the equilibrium constant for the formation reaction is called the **formation constant, K_f**

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$$

Formation Constants

TABLE 16.3 Formation Constants of Selected Complex Ions in Water at 25 °C

Complex Ion	K_f	Complex Ion	K_f
$Ag(CN)_2^-$	1×10^{21}	$Cu(NH_3)_4^{2+}$	1.7×10^{13}
$Ag(NH_3)_2^+$	1.7×10^{7}	$Fe(CN)_6^{4-}$	1.5×10^{35}
$Ag(S_2O_3)_2^{3-}$	3.8×10^{13}	$Fe(CN)_6^{3-}$	2×10^{43}
AlF_6^{3-}	7×10^{19}	$Hg(CN)_4^{2-}$	1.8×10^{41}
$Al(OH)_4^-$	3×10^{33}	$HgCl_4^{2-}$	1.1×10^{16}
$CdBr_4^{2-}$	5.5×10^{3}	HgI_4^{2-}	2×10^{30}
CdI_4^{2-}	2×10^{6}	$Ni(NH_3)_6^{2+}$	2.0×10^{8}
$Cd(CN)_4^{2-}$	3×10^{18}	$Pb(OH)_3^-$	8×10^{13}
$Co(NH_3)_6^{3+}$	2.3×10^{33}	$Sn(OH)_3^-$	3×10^{25}
$Co(OH)_4^{2-}$	5×10^{9}	$Zn(CN)_4^{2-}$	2.1×10^{19}
$Co(SCN)_4^{2-}$	1×10^{3}	$Zn(NH_3)_4^{2+}$	2.8×10^{9}
$Cr(OH)_4^-$	8.0×10^{29}	$Zn(OH)_4^{2-}$	3×10^{15}
$Cu(CN)_4^{2-}$	1.0×10^{25}		

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Ex 16.13 – 200.0 mL of 1.5×10^{-3} M $Cu(NO_3)_2$ is mixed with 250.0 mL of 0.20 M NH_3. What is the $[Cu^{2+}]$ at equilibrium?

Write the formation reaction and K_f expression. Look up K_f value	$Cu^{2+}(aq) + 4\ NH_3(aq) \Leftrightarrow Cu(NH_3)_4^{2+}(aq)$ $K_f = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = 1.7 \times 10^{13}$
Determine the concentration of ions in the diluted solutions	$[Cu^{2+}] = \frac{0.200\text{L} \times \frac{1.5 \times 10^{-3}\text{ mol}}{1\text{L}}}{(0.200\text{L} + 0.250\text{L})} = 6.7 \times 10^{-4}\text{ M}$ $[NH_3] = \frac{0.250\text{L} \times \frac{2.0 \times 10^{-1}\text{ mol}}{1\text{L}}}{(0.200\text{L} + 0.250\text{L})} = 1.1 \times 10^{-1}\text{ M}$

Ex 16.13 – 200.0 mL of 1.5×10^{-3} M $Cu(NO_3)_2$ is mixed with 250.0 mL of 0.20 M NH_3. What is the $[Cu^{2+}]$ at equilibrium?

$$Cu^{2+}(aq) + 4\ NH_3(aq) \Leftrightarrow Cu(NH_3)_2^{2+}(aq$$

$$K_f = \frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4^{2+}]} = 1.7 \times 10^{13}$$

Create an ICE table. Since K_f is large, assume all the Cu^{2+} is converted into complex ion, then the system returns to equilibrium

	$[Cu^{2+}]$	$[NH_3]$	$[Cu(NH_3)_2^{2+}]$
Initial	6.7E-4	0.11	0
Change	$-\approx 6.7E\text{-}4$	-4(6.7E-4)	+ 6.7E-4
Equilibri	x	0.11	6.7E-4

X= the small amt of Cu2+ left in solution

Ex 16.13 – 200.0 mL of 1.5×10^{-3} M $Cu(NO_3)_2$ is mixed with 250.0 mL of 0.20 M NH_3. What is the $[Cu^{2+}]$ at equilibrium?

$$Cu^{2+}(aq) + 4\ NH_3(aq) \Leftrightarrow Cu(NH_3)_4^{2+}(aq)$$

$$K_f = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = 1.7 \times 10^{13}$$

	Cu^{2+}	NH_3	$Cu(NH_3)_4^{2+}$
Initial	x	0.11	6.7E-4
Change	- 6.7E-4	-4(6.7E-4)	+ 6.7E-4
Equilibrium	x	0.11	6.7E-4

Substitute in and solve for x

confirm the "x is small" approximation

$$1.7 \times 10^{13} = \frac{(6.7 \times 10^{-4})}{(x)(0.11)^4}$$

$$x = \frac{(6.7 \times 10^{-4})}{(1.7 \times 10^{13})(0.11)^4} = 2.7 \times 10^{-13}$$

since $2.7 \times 10^{-13} << 6.7 \times 10^{-4}$, the approximation is v

The Effect of Complex Ion Formation on Solubility

- the solubility of an ionic compound containing a metal cation that forms a complex ion increases in the presence of aqueous ligands

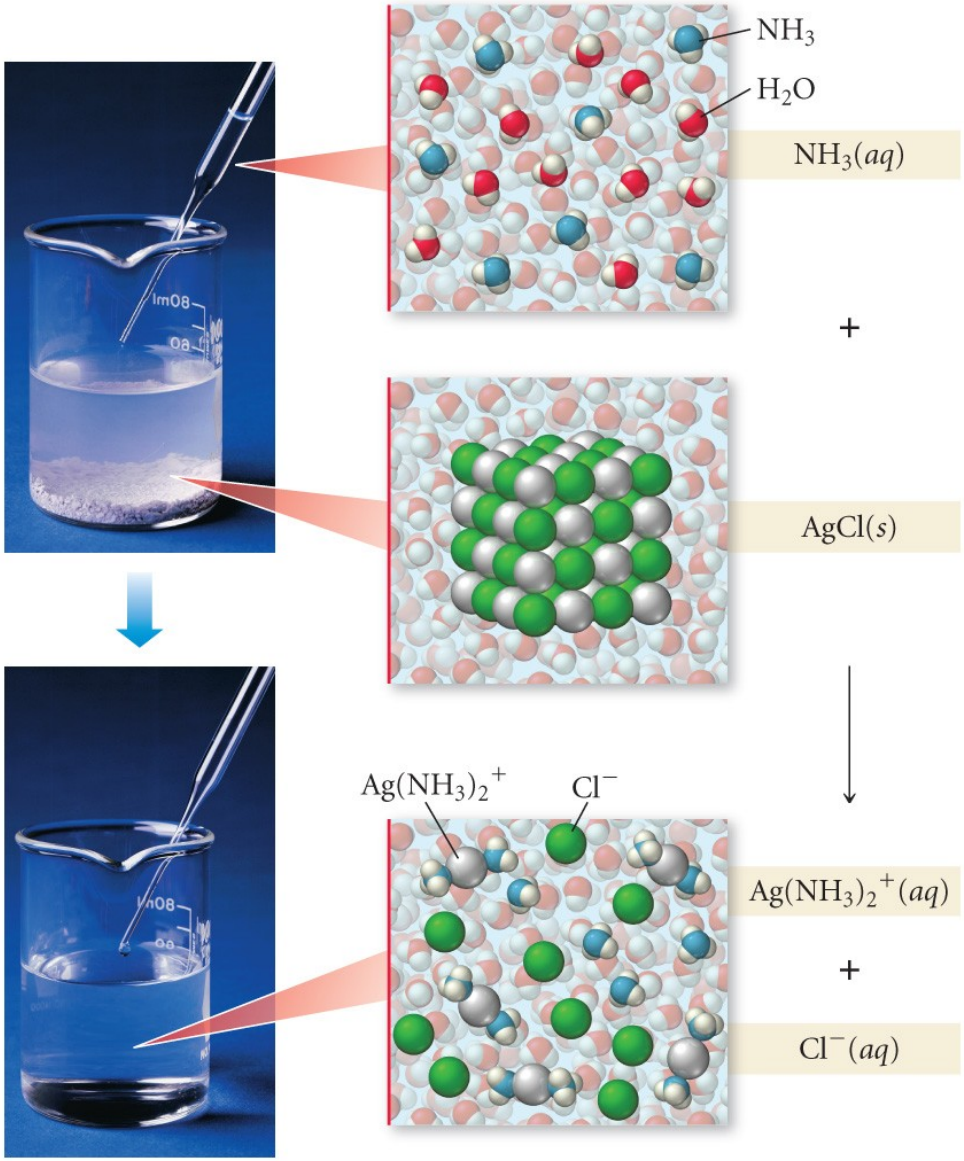
$AgCl_{(s)} \Leftrightarrow Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$ $\quad K_{sp} = 1.77 \times 10^{-10}$

The silver chloride solubility increases due to consumption of the Ag+ ion by NH3 according to LeChatelier's principle as seen by the large formation constant:

$Ag^{+}_{(aq)} + 2\ NH_{3(aq)} \Leftrightarrow Ag(NH_3)_2{}^{+}_{(aq)}$ $\quad K_f = 1.7 \times 10^{7}$

Complex Ion Formation

$$2\,NH_3(aq) + AgCl(s) \rightleftharpoons Ag(NH_3)_2^{+}(aq) + Cl^{-}(aq)$$



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Solubility of Amphoteric Metal Hydroxides

- many metal hydroxides are insoluble
- all metal hydroxides become more soluble in acidic solution
  - ✓ shifting the equilibrium to the right by removing OH^-
- some metal hydroxides also become more soluble in basic solution
  - ✓ acting as a Lewis base forming a complex ion
- substances that behave as both an acid and base are said to be **amphoteric**
- some cations that form amphoteric hydroxides include Al^{3+}, Cr^{3+}, Zn^{2+}, Pb^{2+}, and Sb^{2+}

Al^{3+}

- Al^{3+} is hydrated in water to form an acidic solution

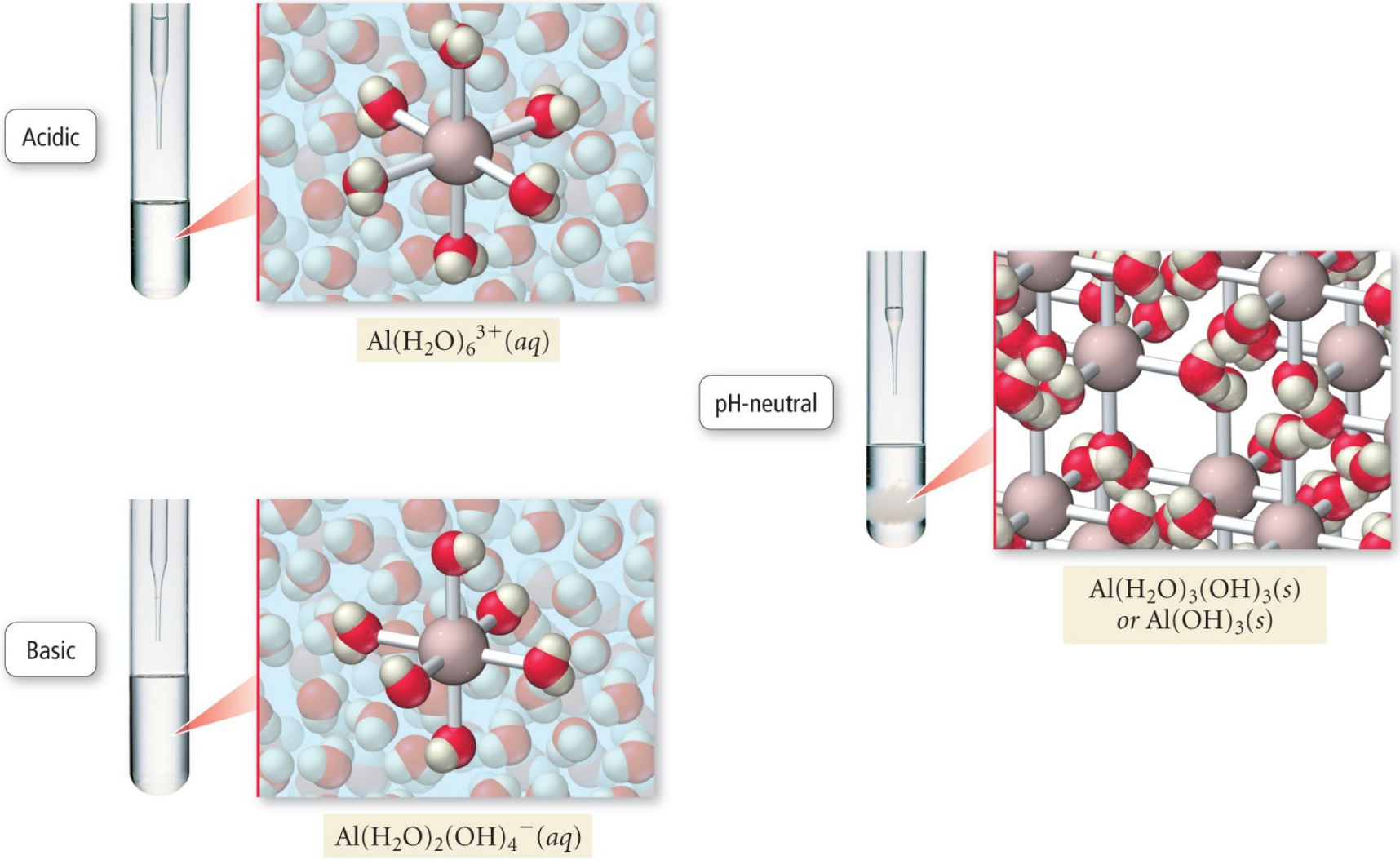
$$Al(H_2O)_6{}^{3+}{}_{(aq)} + H_2O_{(l)} \Leftrightarrow Al(H_2O)_5(OH)^{2+}{}_{(aq)} + H_3O^{+}{}_{(aq)}$$

- addition of OH^- drives the equilibrium to the right and continues to remove H from the molecules

$$Al(H_2O)_5(OH)^{2+}{}_{(aq)} + OH^{-}{}_{(aq)} \Leftrightarrow Al(H_2O)_4(OH)_2{}^{+}{}_{(aq)} + H_2O_{(l)}$$

$$Al(H_2O)_4(OH)_2{}^{+}{}_{(aq)} + OH^{-}{}_{(aq)} \Leftrightarrow Al(H_2O)_3(OH)_{3(s)} + H_2O_{(l)}$$

pH-Dependent Solubility of an Amphoteric Hydroxide



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